

Tutorial 1

The Workhorse: Kohn-Sham DFT

$$\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

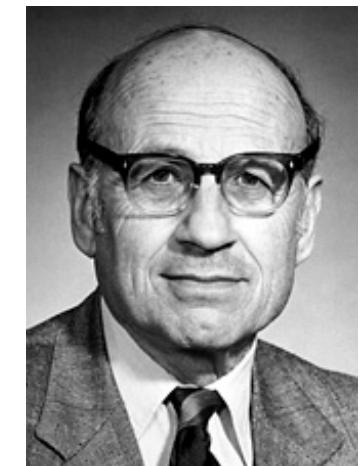
$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (\#\text{grid points})^N$$

5 electrons on a $10 \times 10 \times 10$ grid ~ 10 PetaBytes



$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_i^N \psi_i(\mathbf{r}_i) \quad \rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2$$

$$E[\rho] = T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{\text{xc}}[\rho] + E_Z[\rho] + U[Z]$$



$$\left(-\frac{1}{2}\Delta + V_Z(\mathbf{r}) + V_H[\rho](\mathbf{r}) + V_{\text{xc}}[\rho](\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$E_{\text{xc}}[\rho] = ???$ $V_{\text{xc}}[\rho](\mathbf{r}) = ???$ \rightarrow Approximations: LDA, PBE, ...

An N-electron system: $N \sim 10^{23}$

- Hohenberg-Kohn-Sham DFT takes us a long way

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), \dots, \psi_N(\mathbf{r})\}$$

$$(\#\text{grid points})^N \qquad \qquad N \times (\#\text{grid points})$$

- Nice for atoms and molecules, but in a realistic piece of solid state material we have $O(10^{23})$ electrons!

Translational invariance: Periodic Boundary Conditions

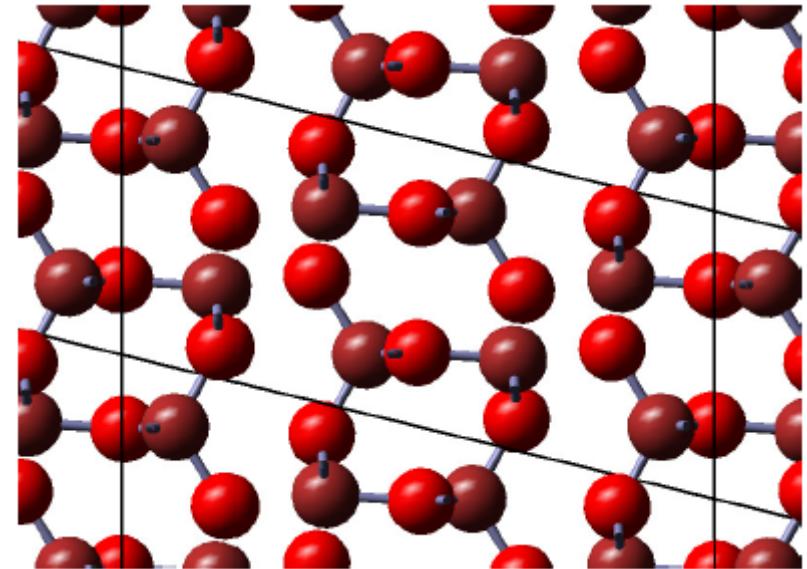
- Translational invariance implies

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \psi_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{R}}$$

and

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$$

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

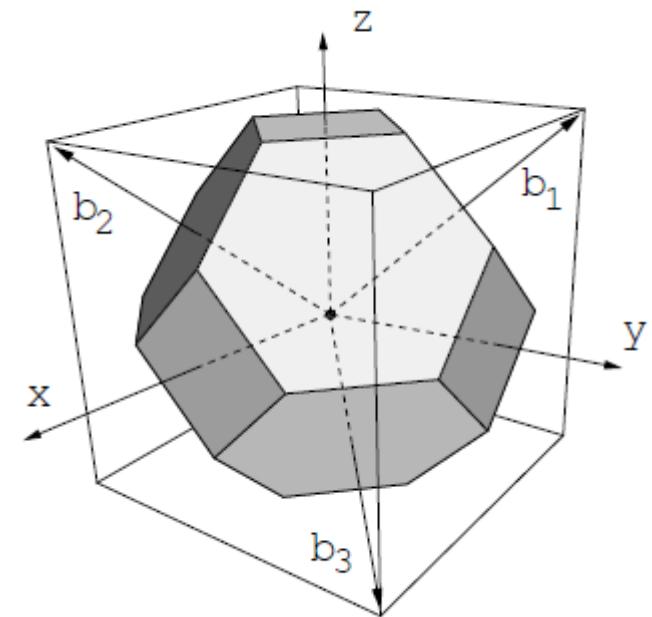
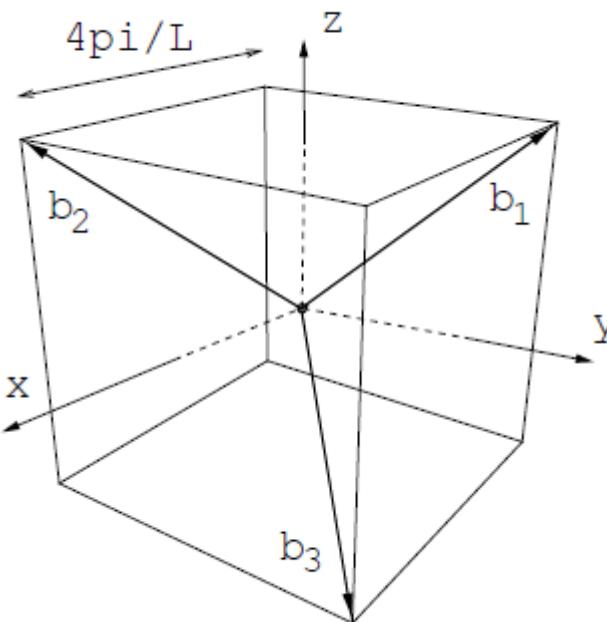
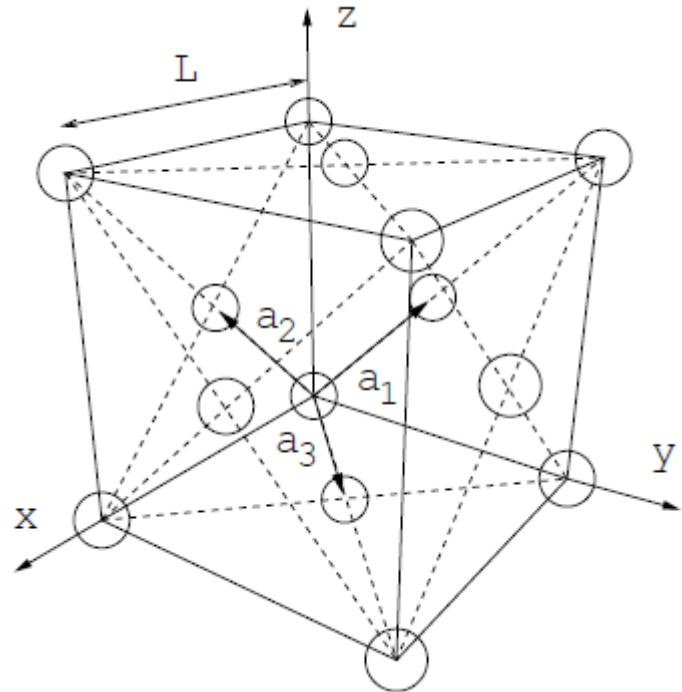


- All states can be labelled by \mathbf{k} and n .

\mathbf{k} is the Bloch wavevector, and is usually constrained to lie within the first Brillouin zone of the reciprocal space lattice.

n is the band index. The number of bands at each \mathbf{k} is of order of the number of electrons per unit cell.

Reciprocal space & the Brillouin Zone



$$\mathbf{b}_1 = \frac{2\pi}{\Omega} \mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{b}_2 = \frac{2\pi}{\Omega} \mathbf{a}_3 \times \mathbf{a}_1 \quad \mathbf{b}_3 = \frac{2\pi}{\Omega} \mathbf{a}_1 \times \mathbf{a}_2$$

$$\Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

- The evaluation of many key quantities, e.g. charge density, density-of-states, and total energy) requires integration over the first BZ. The charge density $\rho(\mathbf{r})$, for instance, is given by

$$\rho(\mathbf{r}) = \frac{1}{\Omega_{\text{BZ}}} \sum_n \int_{\text{BZ}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}$$

- $f_{n\mathbf{k}}$ are the occupation numbers, i.e., the number of electrons that occupy state $n\mathbf{k}$.
- Exploiting the fact that the wave functions at \mathbf{k} -points that are close together will be almost identical, one may approximate the integration over \mathbf{k} by a weighted sum over a discrete set of points

$$\rho(\mathbf{r}) = \sum_n \sum_{\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k},$$

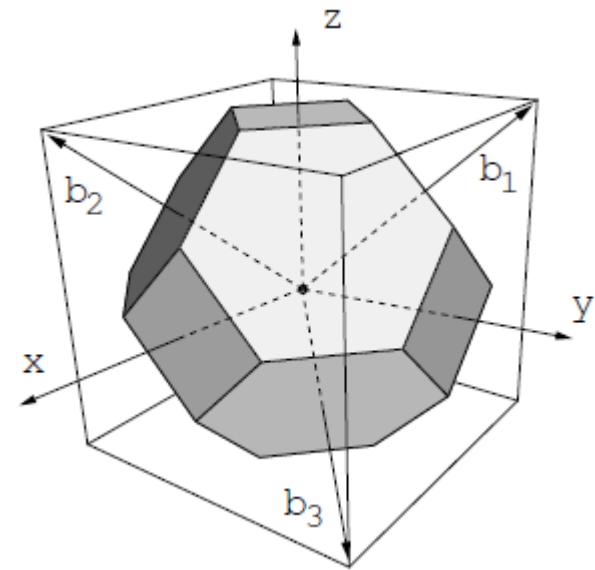
where the weights $w_{\mathbf{k}}$ sum up to one.

Idea: equally spaced mesh in Brillouin-zone.

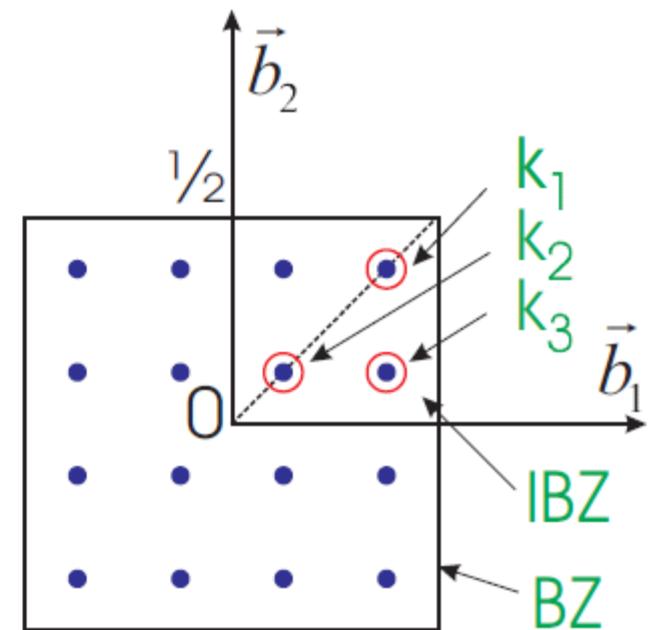
$$\mathbf{k}_{prs} = u_p \mathbf{b}_1 + u_r \mathbf{b}_2 + u_s \mathbf{b}_3$$

$$u_r = \frac{2r - q_r - 1}{2q_r} r = 1, 2, \dots, q_r$$

\mathbf{b}_i reciprocal lattice-vectors
 q_r determines number of k-points in r-direction



- quadratic 2-dimensional lattice
- $q_1 = q_2 = 4 \Rightarrow 16$ k-points
- only 3 inequivalent k-points (\Rightarrow IBZ)
 - $4 \times \mathbf{k}_1 = (\frac{1}{8}, \frac{1}{8}) \Rightarrow \omega_1 = \frac{1}{4}$
 - $4 \times \mathbf{k}_2 = (\frac{3}{8}, \frac{3}{8}) \Rightarrow \omega_2 = \frac{1}{4}$
 - $8 \times \mathbf{k}_3 = (\frac{3}{8}, \frac{1}{8}) \Rightarrow \omega_3 = \frac{1}{2}$



$$\frac{1}{\Omega_{BZ}} \int_{BZ} F(\mathbf{k}) d\mathbf{k} \Rightarrow \frac{1}{4}F(\mathbf{k}_1) + \frac{1}{4}F(\mathbf{k}_2) + \frac{1}{2}F(\mathbf{k}_3)$$

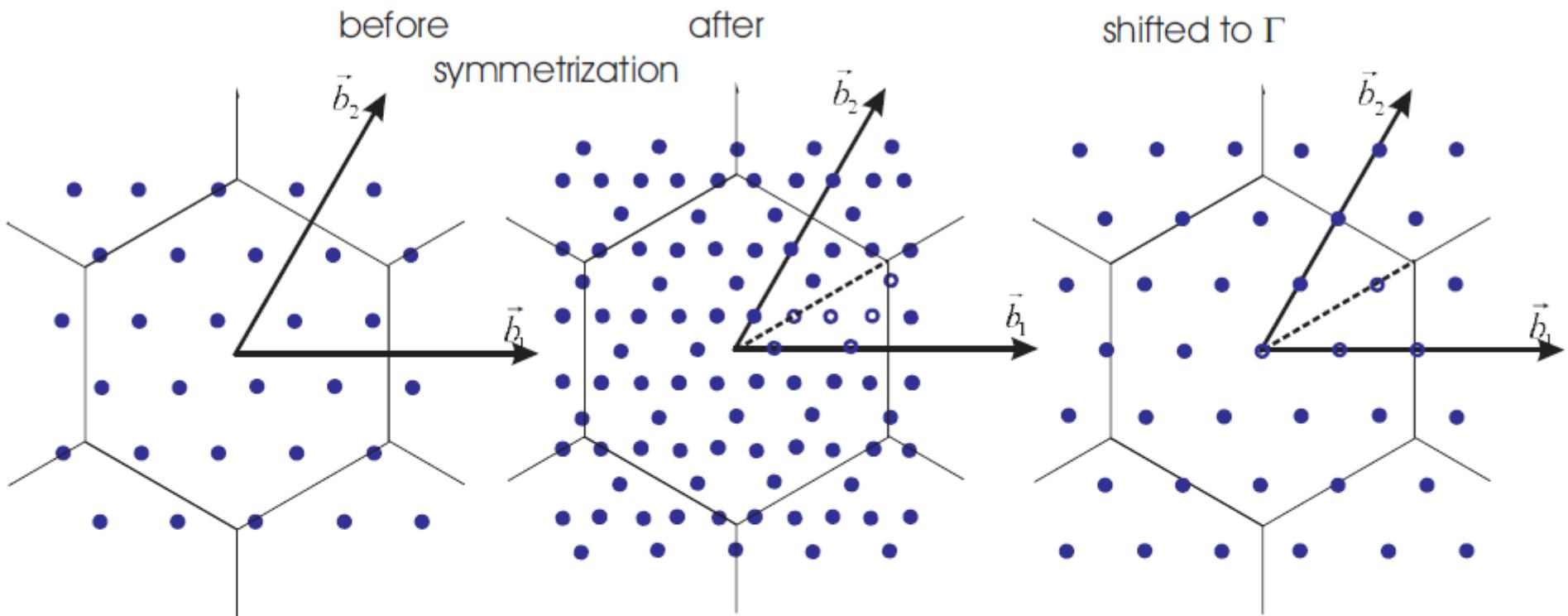
The intractable task of determining $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ (for $N \sim 10^{23}$) has been reduced to calculating $\psi_{n\mathbf{k}}(\mathbf{r})$ at a discrete set of points $\{\mathbf{k}\}$ in the first BZ, for a number of bands that is of the order of the number of electrons *per unit cell*.

Algorithm:

- calculate equally spaced-mesh
- shift the mesh if desired
- apply all symmetry operations of Bravais lattice to all k-points
- extract the irreducible k-points (\equiv IBZ)
- calculate the proper weighting

Common meshes: Two choices for the center of the mesh

- centered on Γ ($\Rightarrow \Gamma$ belongs to mesh).
- centered around Γ . (can break symmetry !!)



- in certain cell geometries (e.g. hexagonal cells) even meshes break the symmetry
- symmetrization results in non equally distributed k-points
- Gamma point centered mesh preserves symmetry

Why use a plane wave basis set

- Historical reason: Many elements exhibit a band-structure that can be interpreted in a free electron picture (metallic s and p elements). Pseudopotential theory was initially developed to cope with these elements (pseudopotential perturbation theory).
- Practical reason: The total energy expressions and the Hamiltonian \mathbf{H} are easy to implement.
- Computational reason: The action $\mathbf{H}|\psi\rangle$ can be efficiently evaluated using FFT's.

The plane wave basis set

- Introduce the cell periodic part $u_{n\mathbf{k}}$ of the wavefunctions

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$$

with $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$.

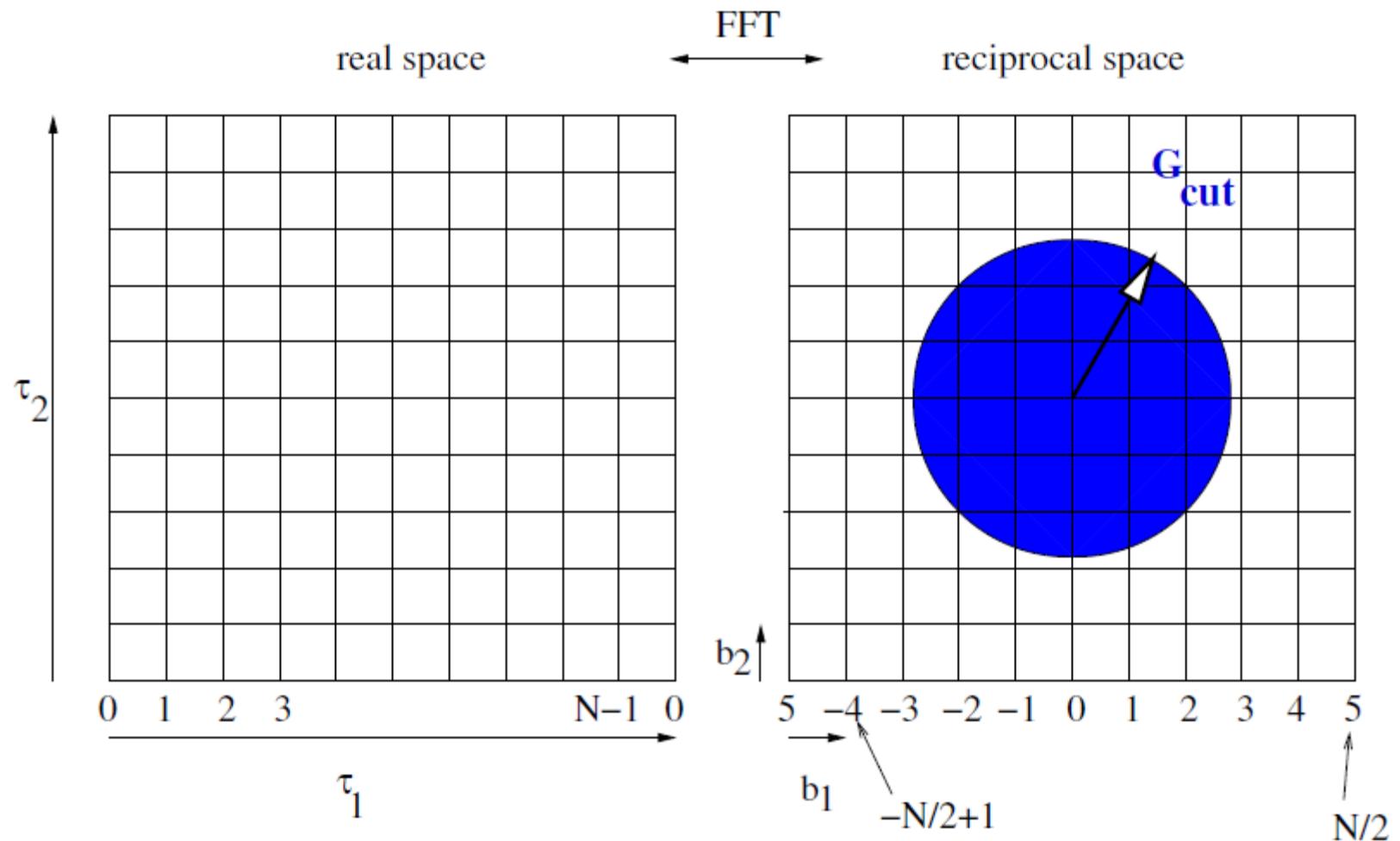
- All cell periodic functions are now written as a sum of plane waves

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{Gr}} \quad \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{Gr}} \quad V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{Gr}}$$

- In practice only those plane waves $|\mathbf{G} + \mathbf{k}|$ are included for which

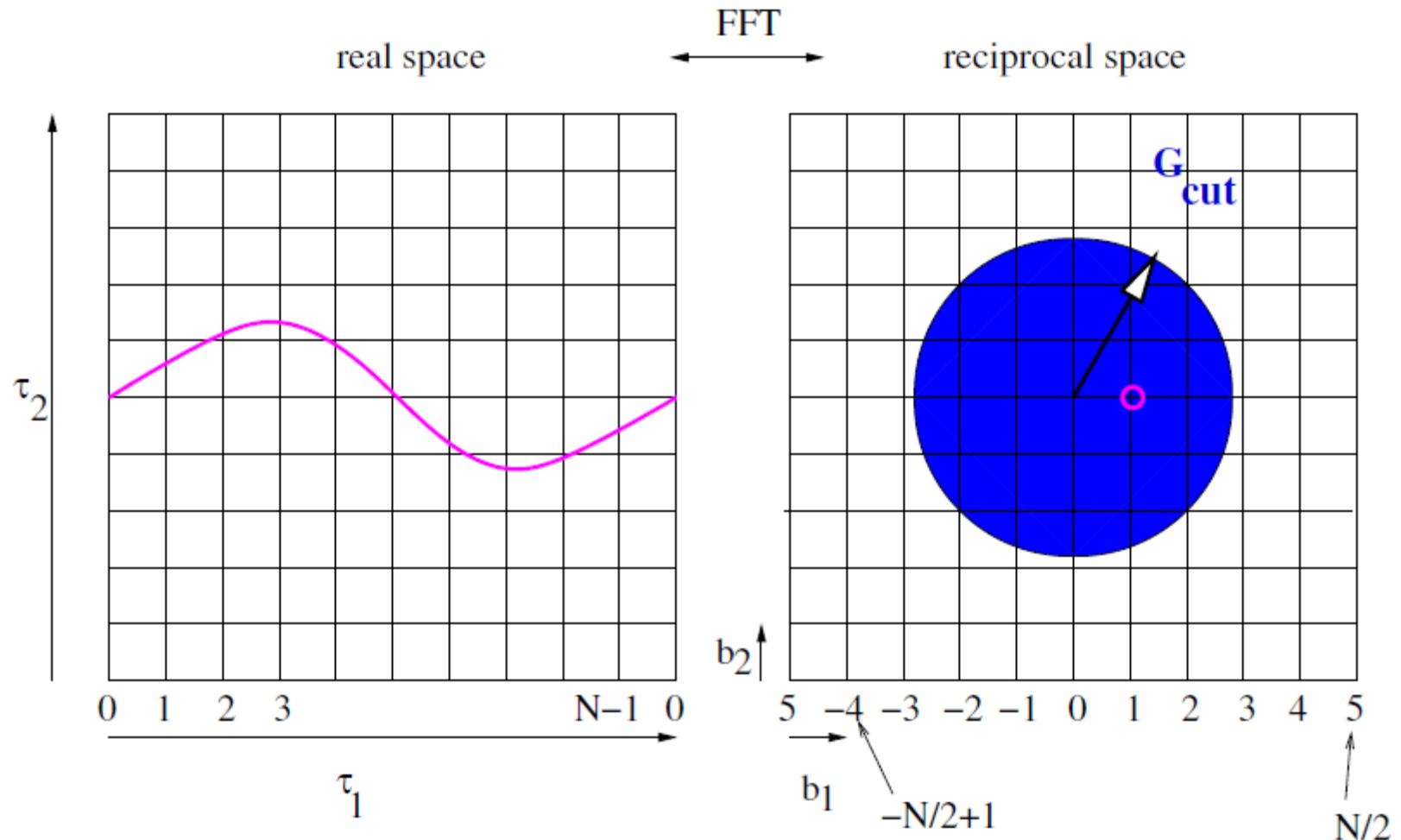
$$\frac{1}{2}|\mathbf{G} + \mathbf{k}|^2 < E_{\text{cutoff}}$$



$$x_1 = n_1 / N \tau_1$$

$$g_1 = n_1 2 \pi / \tau_1$$

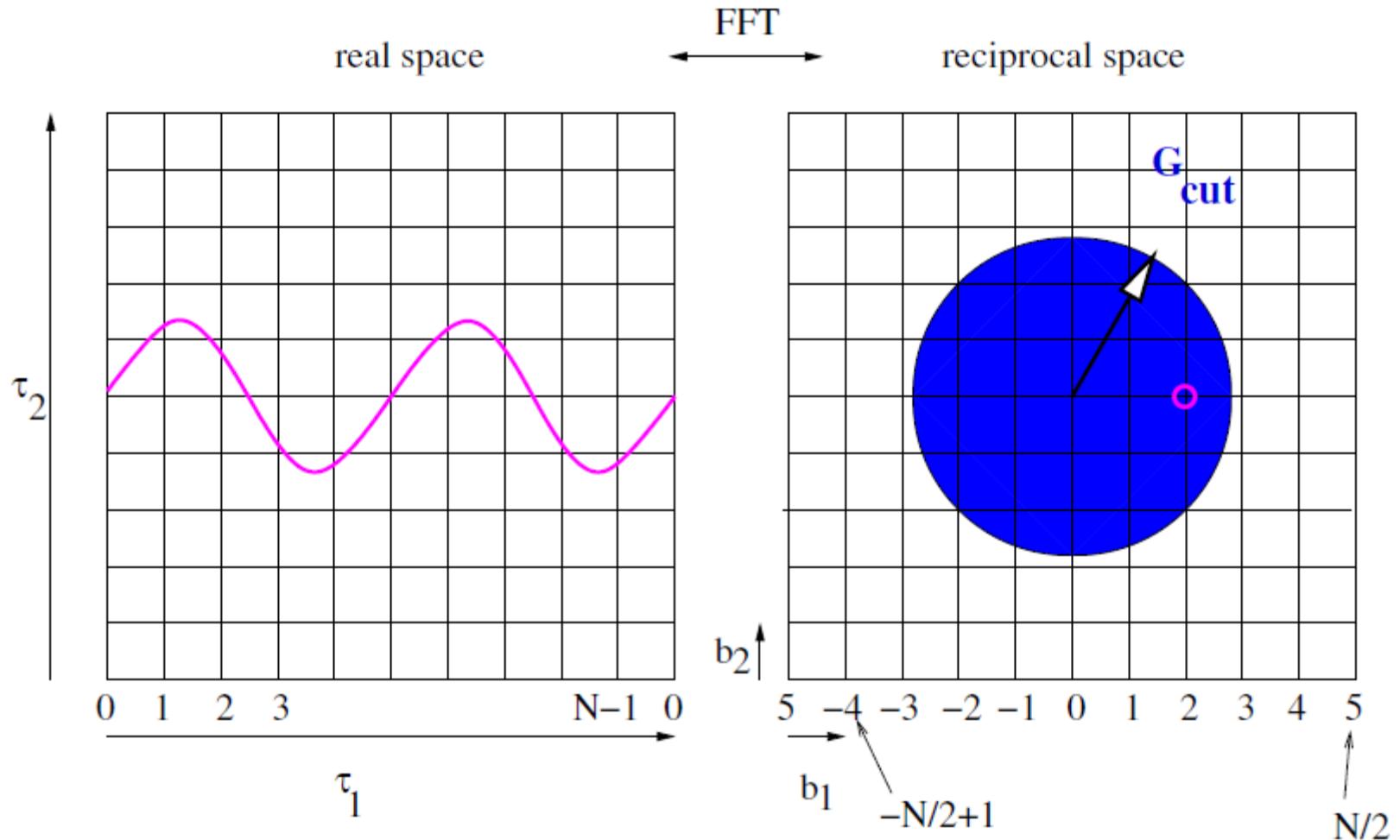
$$C_{rnk} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{Gr}} \quad \xleftrightarrow{\text{FFT}} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{rnk} e^{-i\mathbf{Gr}}$$



$$x_1 = n_1 / N \tau_1$$

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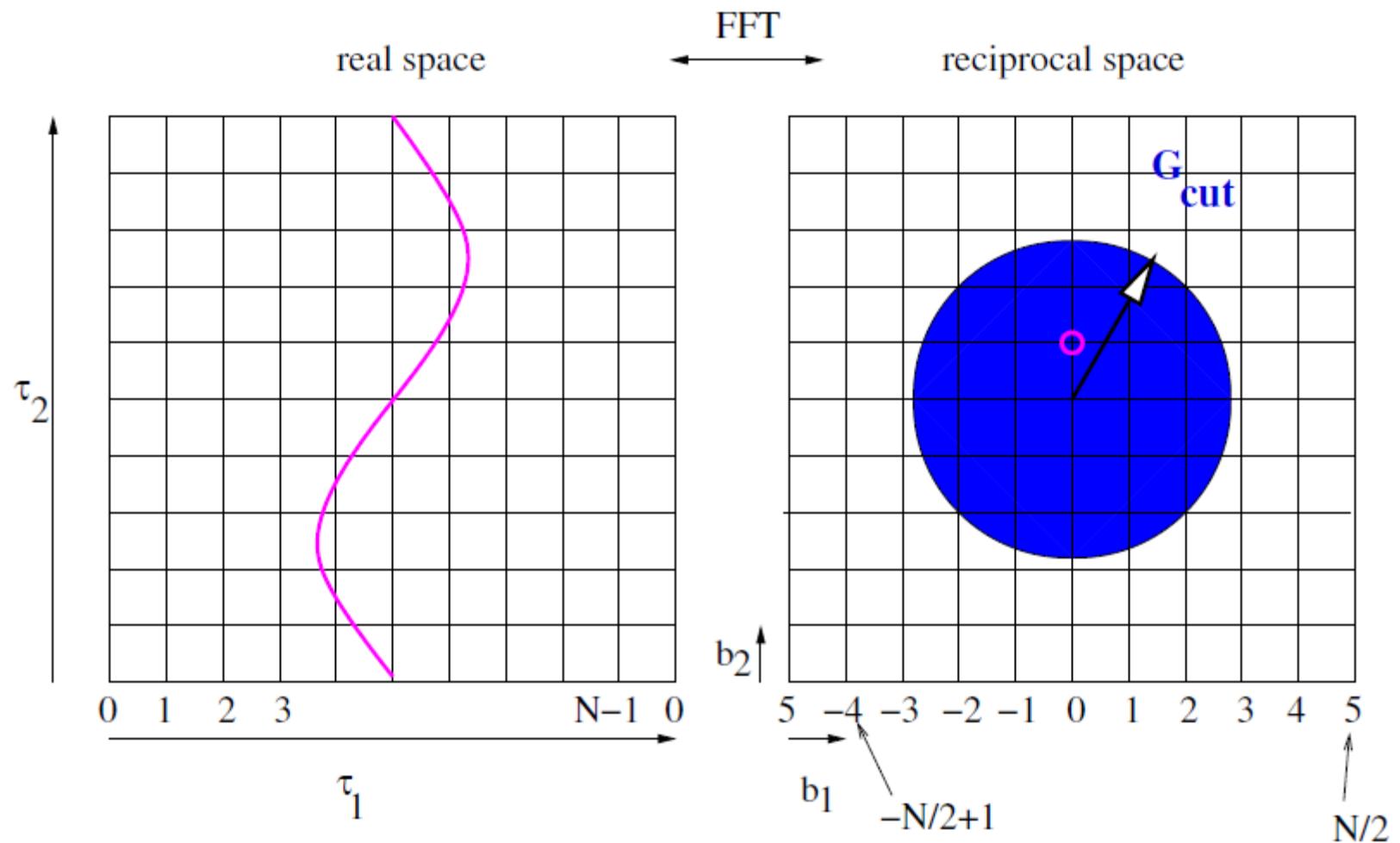
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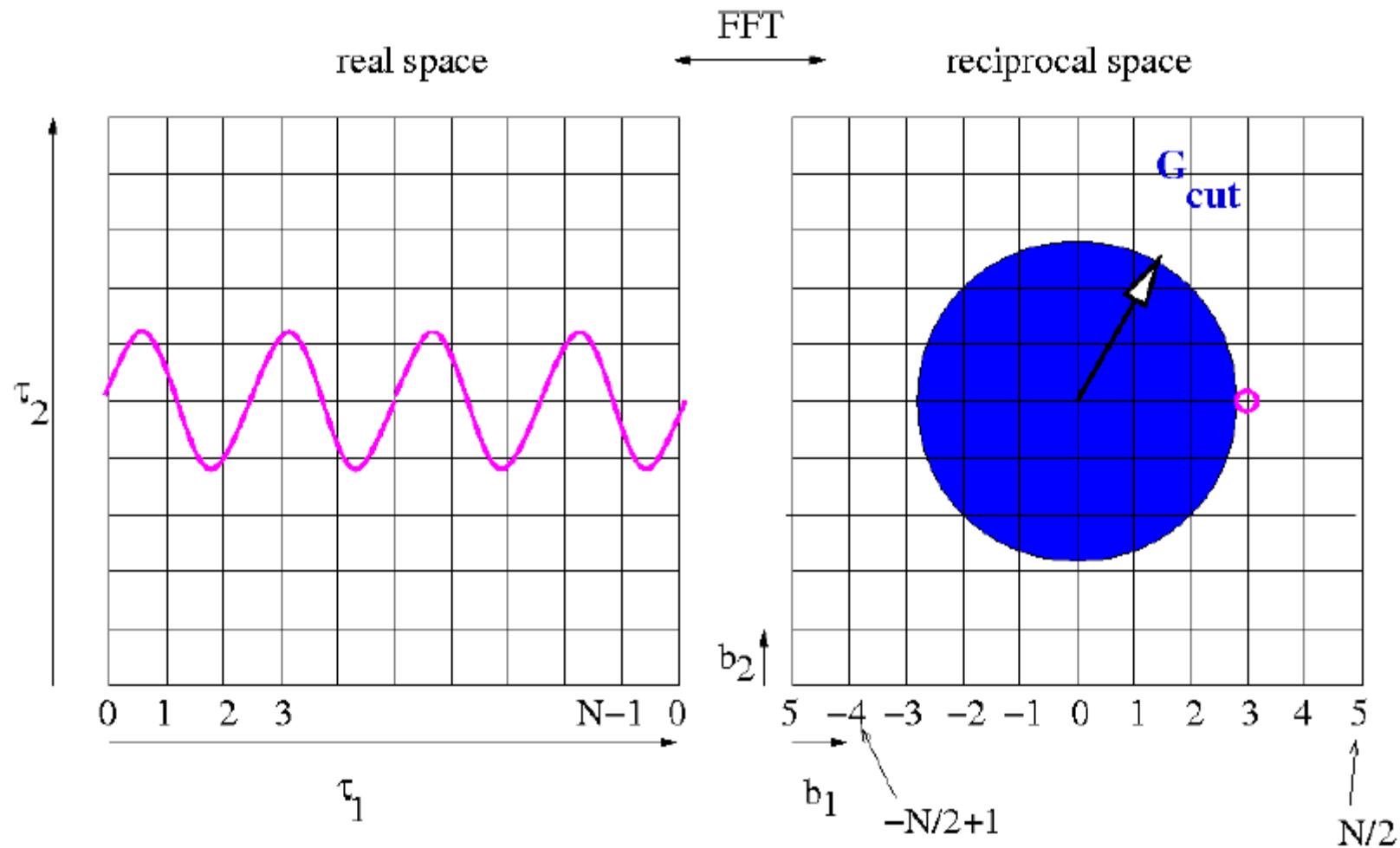
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$$x_1 = n_1 / N \tau_1$$

$$g_1 = n_1 2 \pi / \tau_1$$

$$C_{rnk} = \sum_G C_{Gnk} e^{iGr} \quad \xleftrightarrow{\text{FFT}} \quad C_{Gnk} = \frac{1}{N_{\text{FFT}}} \sum_r C_{rnk} e^{-iGr}$$

Evaluation of $\mathbf{H}|\psi_{n\mathbf{k}}\rangle$

$$\left(-\frac{1}{2}\Delta + V(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r})$$

using the convention

$$\langle \mathbf{r} | \mathbf{G} + \mathbf{k} \rangle = \frac{1}{\Omega^{1/2}} e^{i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}} \rightarrow \langle \mathbf{G} + \mathbf{k} | \psi_{n\mathbf{k}} \rangle = C_{\mathbf{G}n\mathbf{k}}$$

- Kinetic energy:

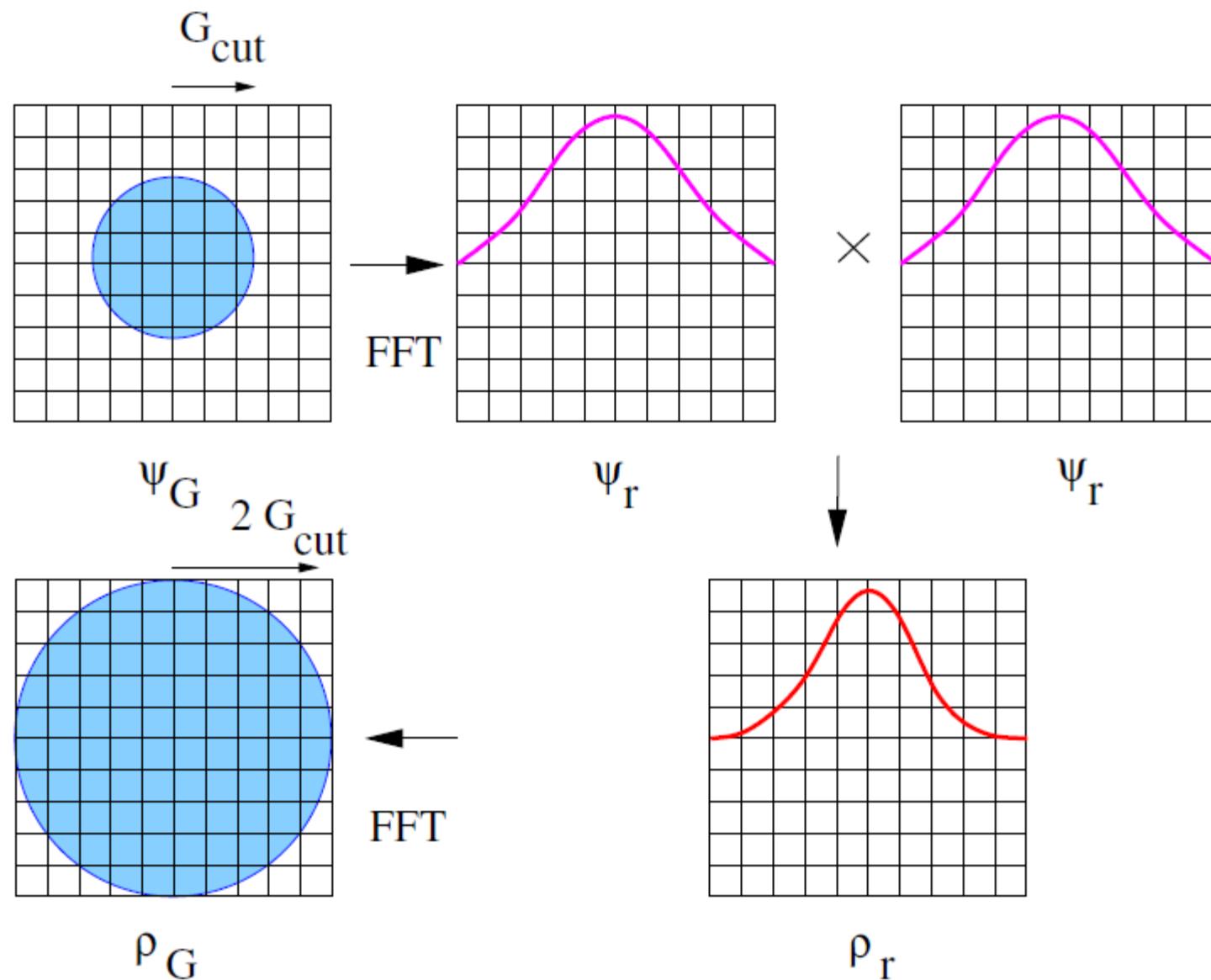
$$\langle \mathbf{G} + \mathbf{k} | -\frac{1}{2}\Delta | \psi_{n\mathbf{k}} \rangle = \frac{1}{2} |\mathbf{G} + \mathbf{k}|^2 C_{\mathbf{G}n\mathbf{k}} \quad N_{\text{NPLW}}$$

- Local potential: $V = V_H[\rho] + V_{xc}[\rho] + V_{\text{ext}}$
 -) Exchange-correlation: easily obtained in real space $V_{\text{xc},\mathbf{r}} = V_{\text{xc}}[\rho_{\mathbf{r}}]$
 -) FFT to reciprocal space $\{V_{\text{xc},\mathbf{r}}\} \rightarrow \{V_{\text{xc},\mathbf{G}}\}$
 -) Hartree potential: Poisson equation in reciprocal space $V_{H,\mathbf{G}} = \frac{4\pi}{|\mathbf{G}|^2} \rho_{\mathbf{G}}$
 -) add all contributions $V_{\mathbf{G}} = V_{H,\mathbf{G}} + V_{\text{xc},\mathbf{G}} + V_{\text{ext},\mathbf{G}}$
 -) FFT to real space $\{V_{\mathbf{G}}\} \rightarrow \{V_{\mathbf{r}}\}$

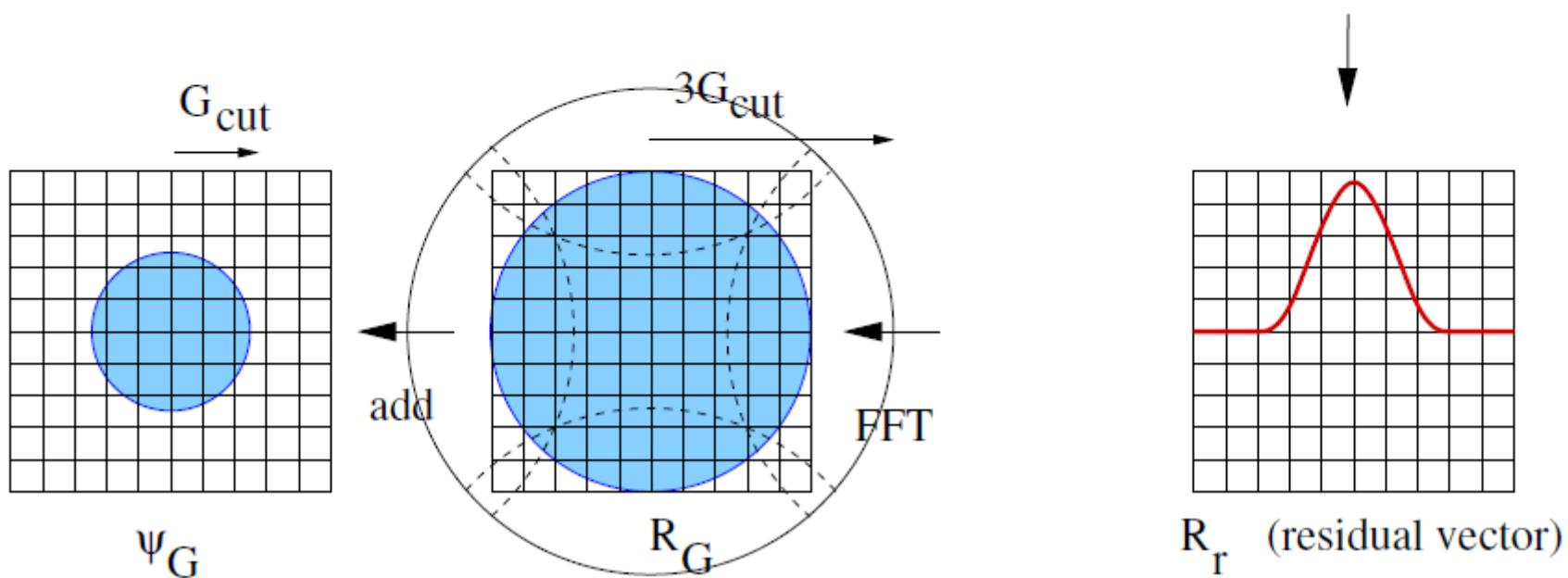
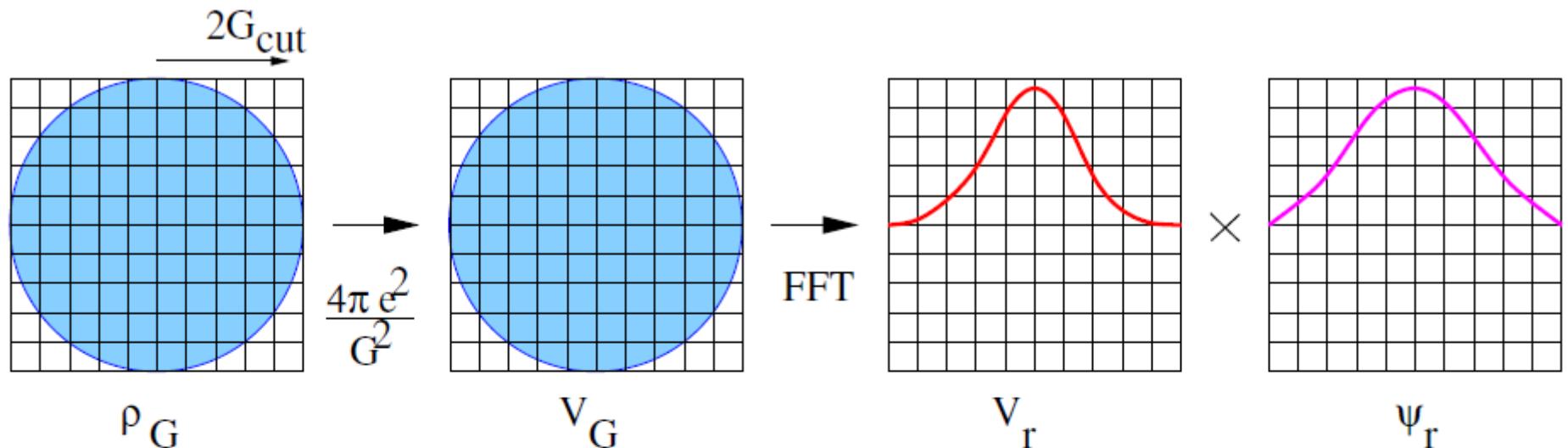
The action

$$\langle \mathbf{G} + \mathbf{k} | V | \psi_{n\mathbf{k}} \rangle = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} V_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\cdot\mathbf{r}} \quad N_{\text{FFT}} \log N_{\text{FFT}}$$

The charge density



The action of the Hamiltonian



I. The INCAR file

Input: I INCAR

- VASP basically uses 4 input files for standard production runs
- INCAR: gives the input parameters which steer the calculation:
- The default values set by VASP itself are a clever choice to do standard calculations
- these standard settings can be modified to specify:
 - what do you want to do? (scf calculation, DOS, dielectric properties ...)
 - give some the basic inputs concerning the required precision, the requested convergence, clever guesses for the input to speed up the convergence ...)

II. The POSCAR file

Input II: POSCAR

```
fcc: Ni
3.53
0.5 0.5 0.0
0.0 0.5 0.5
0.5 0.0 0.5
Ni
1
Selective Dyn
Cartesian
0 0 0 ( T T T)
```

Geometry Input

- header (comment)
- overall scaling constant
- 3-6: Bravais Matrix
- name(s) of the atom(s)
- number of the atoms (of each atom type)
- (optional: selective dynamics)
- Cartesian | Direct
- positions of the atoms

III. The KPOINTS file

Input: III KPOINTS

Automatic mesh

0

G (M)

4 4 4

0. 0. 0.

general format for scf runs...

- ➊ header (comment)
- ➋ $N_{\vec{k}} = 0$: automatic generation scheme
- ➌ Γ -centered (MP) grid
- ➍ # of subdivisions N_i along b_i
- ➎ optional shift of the mesh (s_i)

IV. The POTCAR file

Input: IV POTCAR

- description of the PP
 - data that were required for generating the PP
 - number of valence electrons
 - atomic mass
 - energy cutoff
- if the cell contains different atoms, the atomic POTCARs have to be concatenated, in the same order as the atoms are given in POSCAR
- different XC-types must not be mixed

Output files

OUTCAR

- detailed output of a VASP run, including
 - summary of the input parameters set
 - information about the electronic steps: E_{Fermi} , KS-eigenvalues
 - stress tensors
 - forces on the atoms of each calculation
 - local charges, magnetic moments
 - dielectric properties
- the amount of output written onto OUTCAR can be chosen by setting NWRITE in INCAR

OSZICAR, job.stdout

- gives a short summary of the results
- chosen scf-algorithm
- convergence of the E , charge- and spin densities
- free energies, magnetic moments of the cell

Output files

CONTCAR, XDATCAR

- CONTCAR: updated geometry data *at the end of a run*
 - lattice parameter
 - Bravais matrix
 - ionic positons
 - (velocities)
- the format of CONTCAR is the same as for POSCAR, \Rightarrow it can be used directly for continuation runs after havine been copied to POSCAR)
- XDATCAR: updated ionic positions of each ionic step

DOSCAR,CHGCAR,WAVECAR

- DOSCAR: total DOS and integrated DOS, (local partial DOS)
- CHGCAR: charges ($\rho * V$)
- WAVECAR wavefunction coefficients. WAVECAR can eg be used to continue from a previous run.

Documentation

- The VASP manual (<http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html>)
Index: <http://cms.mpi.univie.ac.at/vasp/vasp/Index.html>
- The VASP wiki (http://cms.mpi.univie.ac.at/wiki/index.php/Main_page)
INCAR-tags: <http://cms.mpi.univie.ac.at/wiki/index.php/Category:INCAR>

Getting started

Assuming you are logged on to “nano.bnl.gov” or “nano2.bnl.gov”!

After logon you'll find yourself in your *home directory*. To find our where that might be, type:

\$ `pwd` (omitting the “\$”-sign)

and you'll get something like

/home3/mmarsman (obviously yours will be different)

Now change to your workspace:

\$ `cd /work/your-username`

and copy the files of the first tutorial to your workspace

\$ `cp -r /software/Workshop14/Tutorials/Tutorial1 .`

end enter the Tutorial1 subdirectory:

\$ `cd Tutorial1`

To get a list of the examples in Tutorial1, type:

\$ `ls`

and you should see something like:

1_10_H2Omd	1_5_CO	2_1_fccSi	2_6_diamondSi_rel
1_1_O_atom	1_6_COvib	2_2_fccSi_dos	2_7_fccNi
1_2_O_atomspin	1_7_COstates	2_3_fccSi_band	
1_3_O_atomspinlowsym	1_8_H2O	2_4_diamondSi	
1_4_Odimer	1_9_H2Ovib	2_5_diamondSi_volrel	

Now change into the directory of the first example:

```
$ cd 1_1_Oatom
```

Another “ls” will list the files that come with the first example:

```
cleanup INCAR job KPOINTS POSCAR POTCAR
```

The files INCAR, KPOINTS, POSCAR, and POTCAR, are input files for VASP.
“cleanup” is a script that you can invoke to remove all output files generated by VASP
(by typing: \$./cleanup)

The “job”-file is what you need to run the example on the computer-cluster.
Before you submit your job, you will need to make a small change in this file!

Type:

```
$ vi job
```

(for those of you who know vi)

or

```
$ nedit job &
```

(for those who don't know vi, or don't want to use it)

or **copy the files to your laptop, edit them there, and copy them back again ...**

N.B.: As of here, lines starting with "#" are interpreted as comments!

```
#!/bin/sh
#PBS -l nodes=1:ppn=4,walltime=10:00
#PBS -N Oatom
#PBS -j oe
#PBS -V

# Workshop participants should use qsub -q cfn_workshop <script>

# note the explicit specification of hardware for operation over two nodes with 8 cores per node
# for smaller jobs, request smaller resources
# for example, to run a serial job, above would read nodes=1:ppn=1

# access to the mvapich mpirun tools
# these lines can go into a resource file for automatic run at login
module load intel/11.1
module load mvapich2/1.5rc1-intel

VASPDIR=/software/Workshop14/bin
# specify the path to the directory where the job should run
WORKDIR=/work/mmarsman/1_1_O_atom
# WORKDIR->YOUR WORK DIRECTORY>

# Count number of nodes from PBS_NODEFILE
NODECOUNT=`sort -u $PBS_NODEFILE | wc -l`

# Count number of processors
PROCCOUNT=`cat $PBS_NODEFILE | wc -l`

# execute Vasp
cd $WORKDIR
cat $PBS_NODEFILE > nodefile.out

mpirun_rsh -ssh -hostfile nodefile.out -n $PROCCOUNT $VASPDIR/vaspPG >> STDOUT
```

Everything in this file is good-to-go, except for "WORKDIR". You will have to specify your working directory here, instead of mine. In this case, this would be something like:

WORKDIR=/work/your-username/Tutorial1/1_1_Oatom

Make the appropriate changes and save and close the file.

You are now ready to submit this job to the “cfn_workshop”-queue of the cluster:

```
$ qsub -q cfn_workshop job
```

(This queue has been specifically set aside for this workshop, so please do not forget the “-q cfn_workshop” option when you submit your jobs)

To check on the status of your job, type:

```
$ qstat -u your-username
```

which should come back with something like:

nano.cfn.bnl.local:									
Job ID	Username	Queue	Jobname	SessID	NDS	TSK	Req'd Memory	Req'd Time	Elap S Time
2129734.nano.cfn	mmarsman	cfn_work	Oatom	--	1	4	--	00:10:00	Q --

where “Q” means it is waiting in the the queue, “R” means running, and “C” it's finished.

If you decide you want to remove your job from the queue, type:

```
$ qdel job-id# (in this case it would be: $ qdel 2129734)
```

When your job is finished you may look at the (human-readable) results using “vi”, “nedit”, or copy the relevant output files to your laptop and use whatever editor you like.

N.B.: For those of you who want to look at the VASP output on their own laptops, please copy OUTCAR and vasprun.xml (for p4vasp), and if available PROCAR to your laptop.

To take a quick look at (small) files you may type:

```
$ cat filename
```

which dumps the contents of the file onto your screen (therfore useless for large files), or

```
$ less filename
```

which allows you to scroll down the file pressing the <space-bar>, and up (down) using the <up-arrow> and <page-up> (<down-arrow> and <page-down>) keys.

Especially “less” might be more convenient than constantly copying stuff to your laptop!

Other commands you'll probably need are:

```
$ cd ..
```

to move “up” one level in your directory tree, and

```
$ cp source destination
```

to copy the file “source” to “destination. For instance “\$ cp OUTCAR ../OUTCAR.bck”, which copies the OUTCAR file in your current directory to OUTCAR.bck one-level up in your directory-tree.

Similarly you may move files by

```
$ mv source destination
```

or remove a file by

```
$ rm filename
```

N.B.: there is no undo!

Another very useful command is “grep” (when you know what you're looking for). After your first run is finished, and you have an OUTCAR try:

and
\$ grep “e e” OUTCAR (beware there are 2 spaces in-between the e's)
\$ grep “y w” OUTCAR (again 2 spaces)

or try for instance:

```
$ grep "E-fermi" OUTCAR
```

Most unix commands come with an online description, a socalled man-page.
If you're interested, type:

```
$ man grep
```

and scroll through the description as you would with “less”.

Important:

If you need to run p4vasp from nano.bnl.gov or nano2.bnl.gov (the head-nodes) then you'll need to export the graphics environment when you establish the ssh-connection, by means of the “-X”-option:

```
$ ssh -X username@ssh.bnl.gov
```

followed by

```
$ ssh -X username@nano.bnl.gov           (same for nano2.bnl.gov)
```

Additionally you'll have to load some p4vasp specific settings on the head-nodes by:

```
$ module load p4vasp
```

After all this you should be able to invoke p4vasp, typing:

```
$ p4v
```

Atoms and molecules

Examples:

- O atom
- O₂ dimer
- CO
- H₂O

Tasks:

- Relaxation
- Vibrational frequencies
- MD

The O atom (Example: 1_1_O_atom)

The POSCAR and INCAR files

- determines the lattice vectors (Bravais lattice) and the coordinates (position of the atoms)
- a single atom POSCAR file:

O atom in a box

```
1.0          ! universal scaling parameters
8.0 0.0 0.0  ! lattice vector  a(1)
0.0 8.0 0.0  ! lattice vector  a(2)
0.0 0.0 8.0  ! lattice vector  a(3)
1           ! number of atoms
cart        ! positions in cartesian coordinates
0 0 0
```

- INCAR steers the calculations:

```
SYSTEM = O atom in a box
ISMEAR = 0
```

The O atom (Example: 1_1_O_atom)

The KPOINTS file

- determines how many k-points are used to sample the Brillouin zone
 - for molecules or atoms only a single k-point is required
- KPOINTS file:

Gamma-point only

```
1           ! one k-point
rec         ! in units of the reciprocal lattice vector
0 0 0 1   ! 3 coordinates and weight
```

- when more k-points are used, only the interaction between the atoms (which should be zero) is described more accurately

The O atom (Example: 1_1_O_atom)

Running vasp

```
vasp.4.6.2 07Jul02
POSCAR found : 1 types and    1 ions
LDA part: xc-table for Pade appr. of Perdew
POSCAR, INCAR and KPOINTS ok, starting setup
WARNING: wrap around errors must be expected
entering main loop
      N      E            dE          d  eps      ncg      rms      rms (c)
DAV:  1  0.39156E+02  0.39157E+02 -0.95953E+02  14  0.335E+0
DAV:  2  0.39499E+01 -0.35207E+02 -0.34385E+02  28  0.480E+0
DAV:  3 -0.15830E+00 -0.41082E+01 -0.39042E+01  14  0.376E+0
DAV:  4 -0.31026E+00 -0.15195E+00 -0.13836E+00  14  0.660E+0
DAV:  5 -0.31321E+00 -0.29544E-02 -0.29502E-02  28  0.907E-0  0.286E-01
DAV:  6 -0.31407E+00 -0.86398E-03 -0.18767E-03  14  0.397E-0  0.142E-01
DAV:  7 -0.31422E+00 -0.14198E-03 -0.21862E-04  14  0.149E-0  0.480E-02
DAV:  8 -0.31427E+00 -0.55085E-04 -0.26453E-05  14  0.469E-0
  1 F= -.31427624E+00 E0= -.16001392E+00  d E =-.308525E+00
writing wavefunctions
```

The O atom (Example: 1_1_O_atom)

OSZICAR and stdout file

initial charge corresponds to the charge of isolated overlapping atoms (POTCAR)
for 4 steps the charge remains fixed, then the charge is updated (rms (c) column)

N iteration count

E total energy

dE change of total energy

d eps change of the eigenvalues (fixed potential)

ncg number of optimisation steps $\mathbf{H}\psi$

rms total residual vector $\sum_{nk} w_k f_{nk} (\mathbf{H} - \varepsilon_{nk}) \psi_{nk}$

rms (c) charge density residual vector

The O atom (Example: 1_1_O_atom)

OUTCAR *file*

individual parts are separated by lines

- first part: reading INCAR, POTCAR, POSCAR
- nearest neighbor distances and analysis of symmetry
- information on what was parsed from INCAR
- verbose job information
- information on lattice, k-points and positions
- information on the basis set (number of plane waves)
- non local pseudopotential information
- information for each electronic step (one line in OSZICAR)

The O atom

```
POTLOK: VPU time      0.93: CPU time      0.93
SETDIJ: VPU time      0.01: CPU time      0.01
EDDAV : VPU time      0.82: CPU time      0.83
DOS    : VPU time      0.00: CPU time      0.00
```

```
-----  
LOOP: VPU time      1.76: CPU time      1.76
```

```
eigenvalue-minimisations : 14
total energy-change (2. order) : 0.3915659E+02 (-0.9595269E+02)
number of electron      6.0000000 magnetization
augmentation part       6.0000000 magnetization
```

Free energy of the ion-electron system (eV)

```
-----  
alpha Z      PSCENC =      0.27135287  
Ewald energy TEWEN =     -91.92708002  
-1/2 Hartree DENC =     -281.84385690  
-V(xc)+E(xc) XCENC =     26.11949869  
PAW double counting =     245.99840262     -247.84808825  
entropy T*S   EENTRO =    -0.18330906  
eigenvalues   EBANDS =    -43.69352752  
atomic energy  EATOM =    432.26319604  
-----  
free energy   TOTEN =    39.15658846 eV
```

```
energy without entropy = 39.33989752  energy(sigma->0) = 39.24824299
```

The O atom (Example: 1_1_O_atom)

- eigenvalues

```
k-point 1 : 0.0000 0.0000 0.0000
band No. band energies occupation
 1 -23.8345 2.00000
 2 -8.8952 1.33333
 3 -8.8952 1.33333
 4 -8.8952 1.33333
 5 -0.4860 0.00000
 6 1.8485 0.00000
 7 1.8486 0.00000
```

- information on charge + some more timing informations

soft charge-density along one line, spin component 1									
	0	1	2	3	4	5	6	7	8
x	5.4925	5.1765	4.3721	3.3741	2.4214	1.6318	1.0341	0.6112	0.3290

The O atom (Example: 1_1_O_atom)

- information on the energy and stress tensor

FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)

free energy TOTEN = -0.314276 eV

energy without entropy= -0.005752 energy(sigma->0) = -0.160014

FORCE on cell ==STRESS in cart. coord. units (eV/reduce length):

Direction	X	Y	Z	XY	YZ	ZX
-----------	---	---	---	----	----	----

Alpha Z	0.27	0.27	0.27			
---------	------	------	------	--	--	--

Ewald	-30.64	-30.64	-30.64	0.00	0.00	0.00
-------	--------	--------	--------	------	------	------

Hartree	93.89	93.89	93.89	0.00	0.00	0.00
---------	-------	-------	-------	------	------	------

E(xc)	-27.94	-27.94	-27.94	0.00	0.00	0.00
-------	--------	--------	--------	------	------	------

Local	-147.85	-147.85	-147.85	0.00	0.00	0.00
-------	---------	---------	---------	------	------	------

n-local	-20.54	-20.54	-20.54	0.00	0.00	0.00
---------	--------	--------	--------	------	------	------

augment	5.55	5.55	5.55	0.00	0.00	0.00
---------	------	------	------	------	------	------

Kinetic	126.50	126.50	126.50	0.00	0.00	0.00
---------	--------	--------	--------	------	------	------

Total -0.77 -0.77 -0.77 0.00 0.00 0.00

in kB -2.41 -2.41 -2.41 0.00 0.00 0.00

external pressure = -2.41 kB Pullay stress = 0.00 kB

- final timing information

The O atom (Example: 1_1_O_atom)

Some comments on this particular run

- the relevant energy for molecules and atoms is energy without entropy

energy without entropy = -0.005752 energy(sigma->0) = -0.160014

three degenerate p orbitals are occupied by 2/3 electrons causing a unphysical electronic entropy

entropy T*S EENTRO = -0.30852464

- a tiny value for SIGMA=0.01 would reduce the entropy but might slow convergence (default is SIGMA=0.2)

SIGMA controls the electronic temperature, which is not a very meaningful quantity for molecules and atoms

- the total energy is found to be essentially zero

VASP subtracts from any calculated energy the energy of the atom in the configuration for which the pseudopotential was generated

all pseudopotentials were generated using non spin polarized reference atoms

The O atom (Example: 1_1_O_atom)

Restart vasp in same directory

```
vasp.4.6.2 07Jul02
POSCAR found : 1 types and 1 ions
LDA part: xc-table for Pade appr. of Perdew
found WAVECAR, reading the header
POSCAR, INCAR and KPOINTS ok, starting setup
WARNING: wrap around errors must be expected
the WAVECAR file was read sucessfully
initial charge from wavefunction
entering main loop
      N      E          dE          d eps      ncg      rms      rms (c)
DAV:  1 -0.314277E+00 -0.31428E+00 -0.14320E-06  14  0.899E-03  0.157E-03
DAV:  2 -0.314277E+00  0.64237E-07 -0.19000E-07   7  0.353E-03
      1 F= -.31427731E+00 E0= -.16001499E+00  d E =-.308525E+00
writing wavefunctions
```

when vasp is restarted the **WAVECAR** file is read and the run is continued from the previous wavefunctions (converging rapidly)

The O atom (Example: 1_2_O_atomspin)

Spin polarized calculation

- the O atom is an open shell system with 2 unpaired electrons
- add ISPIN=2 to the INCAR file remove WAVECAR and restart vasp

```
vasp.4.6.2 07Jul02
POSCAR found : 1 types and    1 ions
...
entering main loop
      N      E          dE        d eps      ncg      rms      rms (c)
DAV:   1  0.38975372E+02  0.38975E+02 -0.10098E+03   32  0.259E+02
DAV:   2  0.31791299E+01 -0.35796E+02 -0.35789E+02   64  0.438E+01
DAV:   3 -0.11905610E+01 -0.43697E+01 -0.36660E+01   32  0.327E+01
DAV:   4 -0.12616637E+01 -0.71103E-01 -0.69167E-01   32  0.508E+00
DAV:   5 -0.12625234E+01 -0.85968E-03 -0.85961E-03   48  0.504E-01  0.653E+00
...
DAV:  11 -0.16719490E+01  0.16543E-04 -0.47746E-04   32  0.131E-01
  1 F= -.16719490E+01 E0= -.15948179E+01 d E =-.154262E+00 mag= 1.9986
writing wavefunctions
```

The O atom (Example: 1_2_O_atomspin)

Spin polarized calculation

- eigenstates for spin up and spin down are calculated “separately”
in LSDA they interact only via the effective local potential
spin-up and spin-down potential
- in the OUTCAR file, one can see two spin components
- the spin component 1 has 2 more electrons corresponding the a magnetization of $2 \mu_B$

k-point	1 :	0.0000	0.0000	0.0000
band No.	band energies	occupation		
1	-25.0761	1.00000		
2	-10.0715	1.00000		
3	-10.0715	1.00000		
4	-10.0715	1.00000		
5	-0.3997	0.00000		
6	1.6965	0.00000		
7	1.9499	0.00000		
8	1.9499	0.00000		

spin component 2				
k-point	1 :	0.0000	0.0000	0.0000
band No.	band energies	occupation		
1	-21.8260	1.00000		
2	-7.0425	0.33333		
3	-7.0425	0.33333		
4	-7.0425	0.33333		
5	-0.4479	0.00000		
6	1.9043	0.00000		
7	1.9043	0.00000		
8	1.9043	0.00000		

The O atom (Example: 1_3_O_atomspinlowsym)

Symmetry broken O atom

- in the GGA, most atoms are characterized by a symmetry broken solution
VASP however symmetrizes the charge-density according to the determined symmetry of the cell
check the OUTCAR file, which symmetry is VASP using
- to lower the symmetry simply change the lattice parameters to 7.0 8.0 and 9.0 in the POSCAR file:

```
7.0 0.0 0.0 ! lattice vector a(1)
0.0 7.5 0.0 ! lattice vector a(2)
0.0 0.0 8.0 ! lattice vector a(3)
```

and reduce SIGMA to SIGMA=0.01 (INCAR file)

- rerunning VASP you will find a much lower energy

```
vasp.4.6.2 07Jul02
...
DAV: 17 -0.190131780202E+01 -0.53122E-04 -0.35327E-06 32 0.128E-02
1 F= -.19013178E+01 E0= -.19013178E+01 d E =-.938468E-52 mag= 1.9997
```

The O₂ dimer (Example: 1_4_Odimer)

- POSCAR:

```
0 atom in a box
 1.0          ! universal scaling parameters
 8.0 0.0 0.0  ! lattice vector a(1)
 0.0 8.0 0.0  ! lattice vector a(2)
 0.0 0.0 8.0  ! lattice vector a(3)
2          ! number of atoms
cart        ! positions in cartesian coordinates
 0 0 0          ! first atom
 0 0 1.22       ! second atom
```

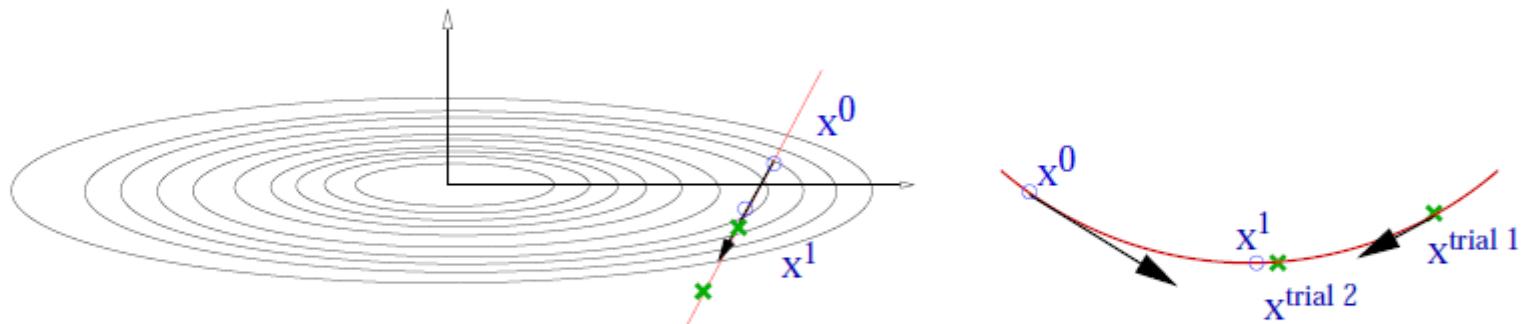
- INCAR:

```
SYSTEM = O2 dimer in a box
ISMEAR = 0 ! Gaussian smearing
ISPIN  = 2 ! spin polarized calculation
NSW    = 5 ! 5 ionic steps
IBRION = 2 ! use the conjugate gradient algorithm
```

The O₂ dimer (Example: 1_4_Odimer)

Relaxing the O₂ dimer

- we have inserted that geometry relaxation should be performed:
in this case 5 ionic steps (NSW = 5) should be done at most
for the relaxation a conjugate gradient algorithm is used IBRION = 2
- CG requires a line minimizations along the search direction



this is done using a variant of Brent's algorithm

- trial step along search direction (gradient scaled by POTIM)
- quadratic or cubic interpolation using energies and forces at \vec{x}_0 and \vec{x}_1 allows to determine the approximate minimum
- continue minimization, if app. minimum is not accurate enough

The O₂ dimer (Example: 1_4_Odimer)

Relaxing the O₂ dimer

```
DAV:   1      0.511277926223E+02      0.51128E+02     -0.31305E+03      60      0.528E+02
...
DAV:  11     -0.985454093746E+01     -0.88826E-04     -0.59757E-05      44      0.746E-02
    1 F= -.98545409E+01 E0= -.98545409E+01 d E =-.985454E+01 mag=      2.0000
curvature:  0.00 expect dE= 0.000E+00 dE for cont linesearch 0.000E+00
trial: gam= 0.00000 g(F)=  0.111E+00 g(S)=  0.000E+00 ort = 0.000E+00 (trialstep = 0.100E+01)
search vector abs. value=  0.111E+00
bond charge predicted
...
    2 F= -.96306943E+01 E0= -.96306943E+01 d E =0.223847E+00 mag=      2.0000
trial-energy change:  0.223847 1 .order  0.186756  -0.110518  0.484030
step:  0.1406(harm=  0.1859) dis= 0.00726 next Energy=  -9.862210 (dE=-0.767E-02)
bond charge predicted
...
    3 F= -.98624278E+01 E0= -.98624278E+01 d E =-.788682E-02 mag=      2.0000
curvature: -0.09 expect dE=-0.448E-05 dE for cont linesearch -0.448E-05
trial: gam= 0.00000 g(F)=  0.484E-04 g(S)=  0.000E+00 ort =-0.231E-02 (trialstep = 0.828E+00)
search vector abs. value=  0.484E-04
reached required accuracy - stopping structural energy minimisation
```

The O₂ dimer (Example: 1_4_Odimer)

CG: What does all this mean?

- the quantity trial-energy change is the change of the energy in the trial step
- the first value after 1. order is the expected energy change calculated from the forces $((\mathbf{F}(\text{start}) + \mathbf{F}(\text{trial}))/2 \times \text{change of positions})$
central difference
second and third value corresponds to $\mathbf{F}(\text{start}) \times \text{change of positions}$ and $\mathbf{F}(\text{trial}) \times \text{change of positions}$
- the value step: is the estimated size of the step leading to a line minimization along the current search direction
harm is the optimal step using a second order (or harmonic) interpolation
- the trial step size can be controlled by the parameter POTIM
the value **step:** times the present POTIM is usually optimal
- the final positions after the optimisation are stored in CONTCAR
you can copy CONTCAR to POSCAR and continue the relaxation

The CO molecule (Example: 1_5_CO)

- POSCAR:

```
...
1 1          ! number of atoms for each species
cart         ! positions in cartesian coordinates
0 0 0        ! first atom
0 0 1.12     ! second atom
```

- POTCAR is created by the concatenation of two individual POTCAR files corresponding to O and C; e.g.:

```
cat  .../O/POTCAR  .../C/POTCAR  >POTCAR
```

- a similar relaxation as in the previous case is performed
but in this case more steps are required, since the first estimate for the minimum is not very accurate
the trial steps are much too long (POTIM parameter)

The CO molecule (Example: 1_5_CO)

Relaxing the CO dimer

```
1 F= -.14764188E+02 E0= -.14764188E+02 d E =-.147642E+02
curvature: 0.00 expect dE= 0.000E+00 dE for cont linesearch 0.000E+00
trial: gam= 0.00000 g(F)= 0.822E+00 g(S)= 0.000E+00 ort = 0.000E+00 (trialstep = 0.100E+01)
search vector abs. value= 0.822E+00
...
2 F= -.12657048E+02 E0= -.12657048E+02 d E =0.210714E+01
trial-energy change: 2.107140 1 .order 1.312507 -0.821770 3.446784
step: 0.1925 (harm= 0.1925) dis= 0.02710 next Energy= -14.843291 (dE=-0.791E-01)
...
3 F= -.14747873E+02 E0= -.14747873E+02 d E =0.163154E-01
curvature: -0.10 expect dE=-0.909E-01 dE for cont linesearch -0.909E-01
ZBRENT: interpolating
opt : 0.0929 next Energy= -14.802370 (dE=-0.382E-01)
...
4 F= -.14797047E+02 E0= -.14797047E+02 d E =-.328587E-01
curvature: -0.04 expect dE=-0.341E-03 dE for cont linesearch -0.341E-03
trial: gam= 0.00000 g(F)= 0.844E-02 g(S)= 0.000E+00 ort =-0.833E-01 (trialstep = 0.819E+00)
search vector abs. value= 0.844E-02
reached required accuracy - stopping structural energy minimisation
```

Vibrational frequencies of CO (Example: 1_6_COvib)

- SYSTEM = CO dimer in a box

```
ISMEAR = 0      ! Gaussian smearing
IBRION = 5      ! vibrational spectrum
NFREE = 2       ! use central differences
POTIM = 0.02    ! 0.02 stepwidth
NSW = 1         ! ionic steps must be larger 0 (that's all)
```

- POSCAR:

```
sel              ! selective degrees of freedom are changed
cart             ! positions in cartesian coordinates
0 0 0   F F T  ! first atom
0 0 1.143 F F T ! second atom
```

the selected degrees of freedom are displaced once in the direction \hat{x} and once $-\hat{x}$ by 0.02 Å

in the present case this makes 4 displacements plus the equilibrium positions (i.e. a total of five ionic configurations)

Vibrational frequencies of CO (Example: 1_6_COvib)

SECOND DERIVATIVES (NOT SYMMETRIZED)

	1Z	2Z
1Z	-114.847733	114.847733
2Z	114.305971	-114.305971

Eigenvectors and eigenvalues of the dynamical matrix

1 f =	63.876494 THz	401.347846 2PiTHz	2130.690412 cm-1	264.172038 meV
	X Y Z	dx dy dz		
	0.000000 0.000000 0.000000	0 0 -0.655709		
	0.000000 0.000000 1.143000	0 0 0.755014		
2 f/i=	0.074763 THz	0.469753 2PiTHz	2.493841 cm-1	0.309197 meV
	X Y Z	dx dy dz		
	0.000000 0.000000 0.000000	0 0 -0.755014		
	0.000000 0.000000 1.143000	0 0 -0.655709		

Eigenvectors after division by SQRT(mass)

Eigenvectors and eigenvalues of the dynamical matrix

1 f =	63.876494 THz	401.347846 2PiTHz	2130.690412 cm-1	264.172038 meV
	X Y Z	dx dy dz		
	0.000000 0.000000 0.000000	0 0 -0.163927		
	0.000000 0.000000 1.143000	0 0 0.217854		
2 f/i=	0.074763 THz	0.469753 2PiTHz	2.493841 cm-1	0.309197 meV
	X Y Z	dx dy dz		
...				

Eigenstates of CO (Example: 1_7_COstates)

- the PROCAR file gives valuable information of the character of the one electron states
- LORBIT 10 DOSCAR and 1 decomposed PROCAR file
- LORBIT 11 DOSCAR and 1m decomposed PROCAR file
- we'll use LORBIT=11, and see if we can distinguish p_x and p_z states

Eigenstates of CO (Example: 1_7_COstates)

PROCAR file:

band 3 # energy -11.46549527 # occ. 2.00000000

band 4 # energy -11.46549510 # occ. 2.00000000

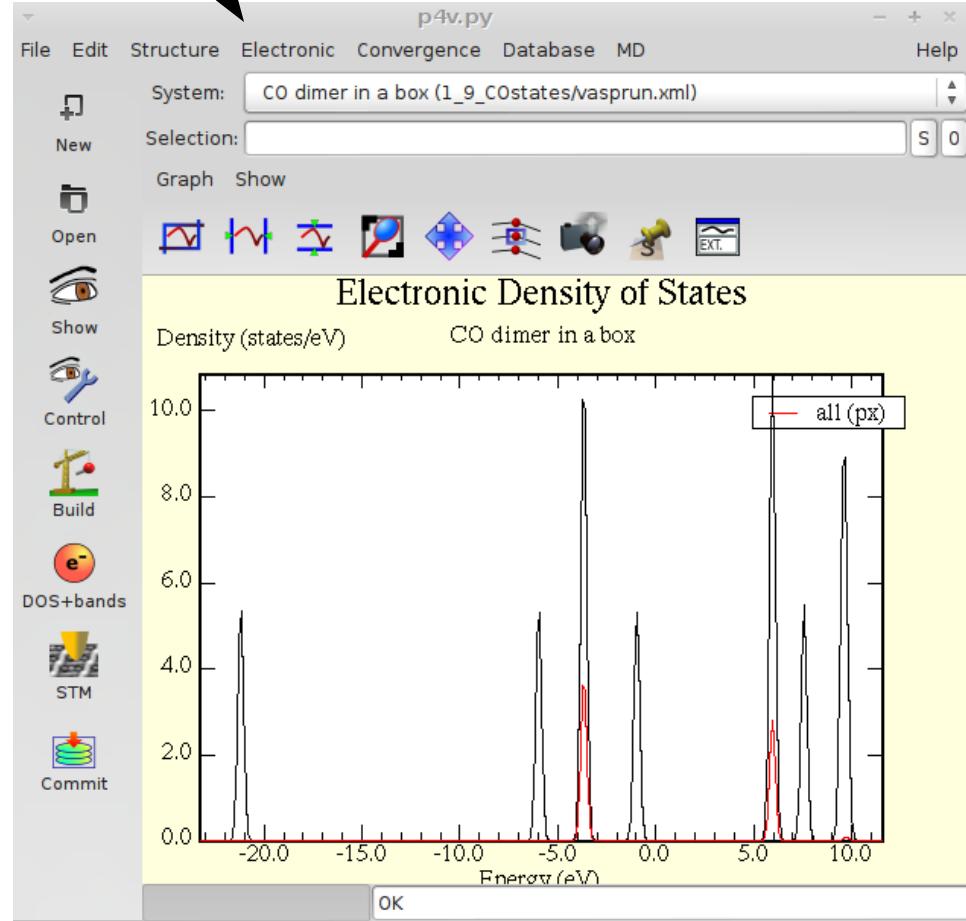
ion	s	py	pz	px	dxy	dyz	dz2	dxz	dx2	tot
1	0.000	0.000	0.000	0.546	0.000	0.000	0.000	0.000	0.000	0.546
2	0.000	0.000	0.000	0.157	0.000	0.000	0.000	0.000	0.000	0.157
tot	0.000	0.000	0.000	0.703	0.000	0.000	0.000	0.000	0.000	0.703

band 5 # energy -8.76451122 # occ. 2.00000000

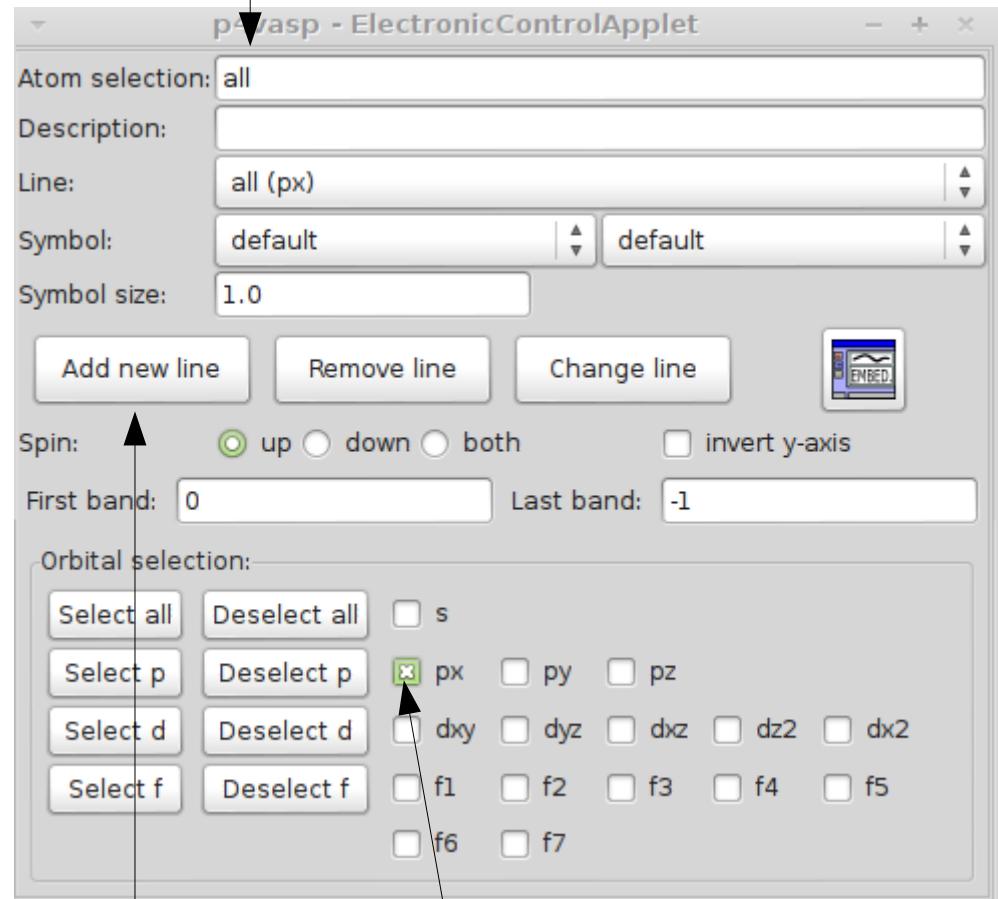
Start p4vasp:

> p4v [vasprun.xml]

Step 1.) go to:
Electronic/Local DOS+bands control



Step 2.) select atoms: "all", "C", "O", "1", "2", ...



Step 3.) select orbital character

Step 4.) and "add new line"

The H₂O molecule (Example: 1_8_H2O)

- POSCAR

```
H2O _2
0.52918 ! scaling parameter
15 0 0
0 15 0
0 0 15
1 2
select
cart
    0.00      0.00      0.00 F F F
    1.10     -1.43      0.00 T T F
    1.10      1.43      0.00 T T F
```

all coordinates are scaled by the factor 0.529

- INCAR:

```
PREC = Normal      ! standard precision
ENMAX = 400        ! cutoff should be set manually
ISMEAR = 0 ; SIGMA = 0.1
IBRION = 1         ! use DIIS algorithm to converge
NFREE = 2          ! 2 independent degrees of freedom
NSW = 10           ! 10 ionic steps
EDIFFG = -0.02     ! forces smaller 0.02 A/eV
```

The H₂O molecule (Relaxation: 1_8_H2O, Vibrations: 1_9_H2Ovib)

- Use PREC = Normal (Default for VASP.5.X)
- I strongly urge to set the energy cutoffs manually in the INCAR file , as it gives you more control over the calculations
- for the ionic optimisation the DIIS algorithm is used
 - this algorithm builds an approximation of the Hessian matrix and converges usually faster than the conjugate gradient algorithm
 - it is however recommended to set the independent degrees of freedom manually
 - EDIFFG determines when to terminate relaxation
 - positive values: energy change between steps must be less than EDIFFG
 - negative values: $|\vec{F}_i| < |\text{EDIFFG}| \quad \forall i = 1, N_{ions}$

MD with the H₂O molecule (Example: 1_10_H2O)

- INCAR:

```
PREC = Normal      ! standard precision
ENMAX = 400        ! cutoff should be set manually
ISMEAR = 0 ; SIGMA = 0.1

IBRION = 0          ! molecular dynamics
NSW = 100           ! 100 steps
POTIM = 1.0          ! timestep 1 fs

SMASS = -3          ! micro-canonical ensemble
TEBEG = 2000 ; TEEND = 2000 ! temperature
```

time step for this system should be around 0.5-0.7 fs

- POSCAR: to save time the box size is reduced to 12 a.u.

- OSZICAR:

```
1 T= 2134. E= -.13655511E+02 F= -.14207209E+02 E0=.. EK= 0.55170E+00 SP= 0.00E+00 SK= 0.00E+00
2 T= 1971. E= -.13643254E+02 F= -.14152912E+02 E0=.. EK= 0.50966E+00 SP= 0.00E+00 SK= 0.00E+00
3 T= 1336. E= -.13629241E+02 F= -.13974630E+02 E0=.. EK= 0.34539E+00 SP= 0.00E+00 SK= 0.00E+00
4 T= 1011. E= -.13624149E+02 F= -.13885486E+02 E0=.. EK= 0.26134E+00 SP= 0.00E+00 SK= 0.00E+00
5 T= 1307. E= -.13629772E+02 F= -.13967549E+02 E0=.. EK= 0.33778E+00 SP= 0.00E+00 SK= 0.00E+00
```

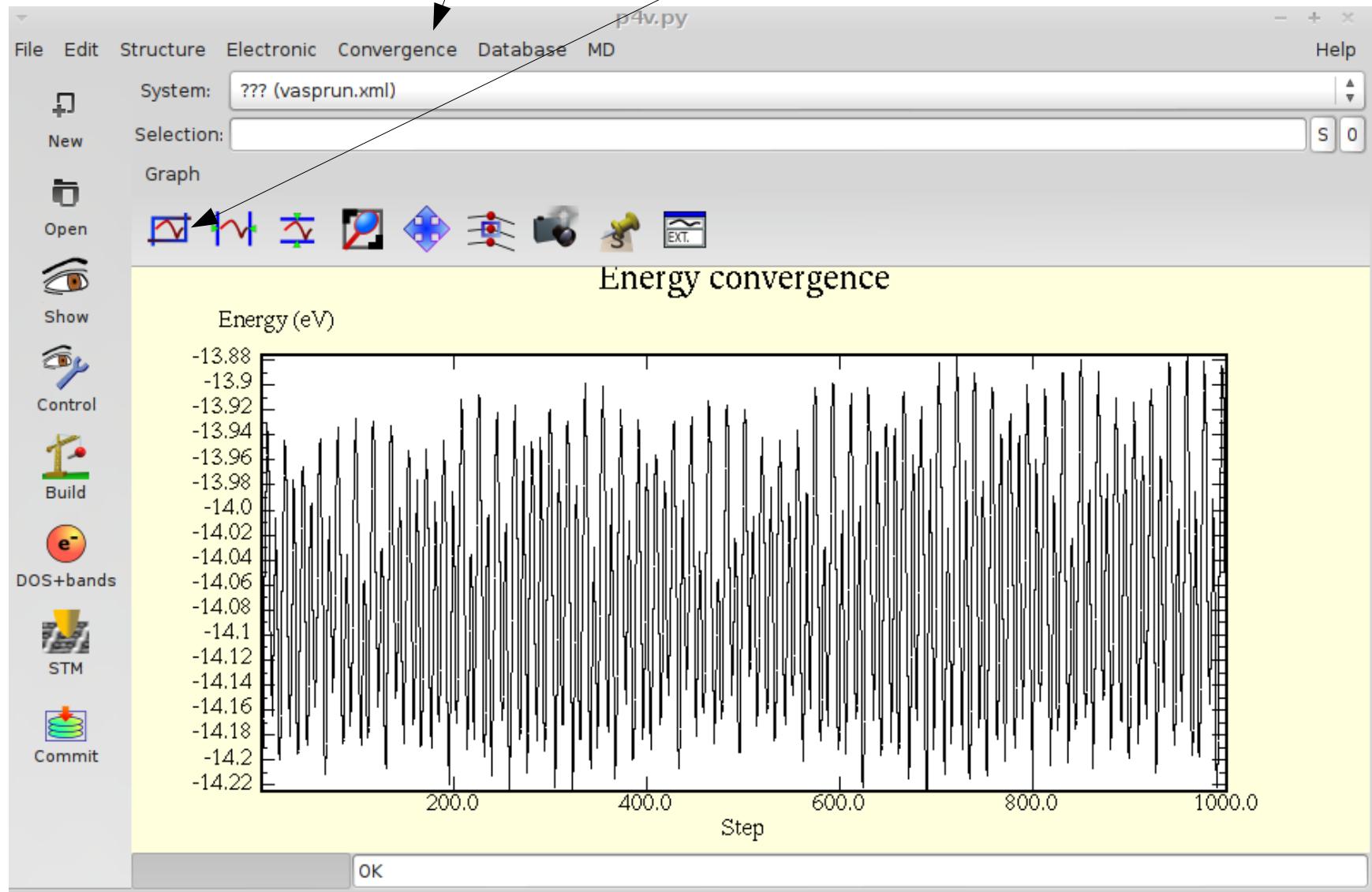
MD with the H₂O molecule (Example: 1_10_H2O)

Start p4vasp:

> p4v [vasprun.xml]

Step 1.) go to: Convergence/Energy

Step 2.) update graph



Further things to try

- How does the energy change when you decrease SIGMA to 0.01 in the INCAR file starting from 0 atom ? Why ?
- Try to copy CONTCAR to POSCAR after running the example O dimer. Why is the calculation so fast ?
- Try to play with the parameter POTIM for the example O dimer. What is the optimal value ?
- What is the reason for the imaginary frequency in the example CO vibration. Does the behavior improve when the step width (smaller or larger) is changed. Also try to improve the precession to which the groundstate is converged (EDIFF=1E-5). What happens if the accuracy of the calculations is improved (PREC=Accurate).
- Try to use the conjugate gradient algorithm to the H₂O molecule (example H2O).
- Calculate the vibrational frequencies of the H₂O molecule (example H2Ovib). Why does one find 3 modes that have small frequencies. Try EDIFF=1E-5 instead of EDIFF=1E-4.

Bulk systems

Examples:

- fcc Si
- fcc Ni

Tasks:

- Equilibrium volume & structure
- Density-of-states (DOS)
- Bandstructure

Equilibrium volume of fcc Si (Example: 2_1_fccSi)

general:

```
System = fcc Si  
ISTART = 0 ; ICHARG=2  
ENCUT = 240  
ISMEAR = 0; SIGMA = 0.1;
```

K-Points

```
0  
Monkhorst Pack  
11 11 11  
0 0 0
```

INCAR

- startjob; initial charge-density from overlapping atoms
- energy cut-off: 240 eV (from POTCAR)

KPOINTS

- equally spaced mesh
- odd → centered on Γ
- results in 56 k-points in IBZ

Equilibrium volume of fcc Si (Example: 2_1_fccSi)

fcc Si:

3.9

0.5 0.5 0.0

0.0 0.5 0.5

0.5 0.0 0.5

1

cartesian

0 0 0

files used in this example:

POTCAR KPOINTS INCAR

POSCAR

POSCAR

- fcc Si lattice constant 3.9 Å
- 1 atom in cell

groundstate volume ?

- calculate energy for different lattice parameters
- fit to some equation of states to obtain the equilibrium volume

Equilibrium volume of fcc Si (Example: 2_1_fccSi)

Automated volume scan (by means of a shell script):

```
#!/bin/bash
BIN=<some VASP executable>
rm WAVECAR
for i in 3.5 3.6 3.7 3.8 3.9 4.0 4.1 4.2 4.3 ; do
cat >POSCAR <<!
fcc:
    $i
    0.5 0.5 0.0
    0.0 0.5 0.5
    0.5 0.0 0.5
    1
cartesian
0 0 0
!
echo "a= $i" ; $BIN
E='tail -1 OSZICAR' ; echo $i $E >>SUMMARY.fcc
done
cat SUMMARY.fcc
```

loop.job

- Unix bash script
- use lattice parameters from 3.5 to 4.3 Å
- Result in SUMMARY.fcc

Equilibrium volume of fcc Si (Example: 2_1_fccSi)

```
3.4 1 F= -.40916606E+01 E0= -.40915302E+01 d E =-.260877E-03
3.5 1 F= -.44301421E+01 E0= -.44278642E+01 d E =-.455582E-02
3.6 1 F= -.46635511E+01 E0= -.46621165E+01 d E =-.286909E-02
3.7 1 F= -.47986983E+01 E0= -.47966436E+01 d E =-.410940E-02
3.8 1 F= -.48654598E+01 E0= -.48639627E+01 d E =-.299421E-02
3.9 1 F= -.48784931E+01 E0= -.48769634E+01 d E =-.305944E-02
4.0 1 F= -.48498418E+01 E0= -.48492073E+01 d E =-.126898E-02
4.1 1 F= -.47865540E+01 E0= -.47857796E+01 d E =-.154878E-02
4.2 1 F= -.46948550E+01 E0= -.46934142E+01 d E =-.288164E-02
4.3 1 F= -.45840107E+01 E0= -.45820708E+01 d E =-.387967E-02
4.4 1 F= -.44618699E+01 E0= -.44599101E+01 d E =-.391948E-02
```

SUMMARY.fcc

- Energy vs. lattice parameter

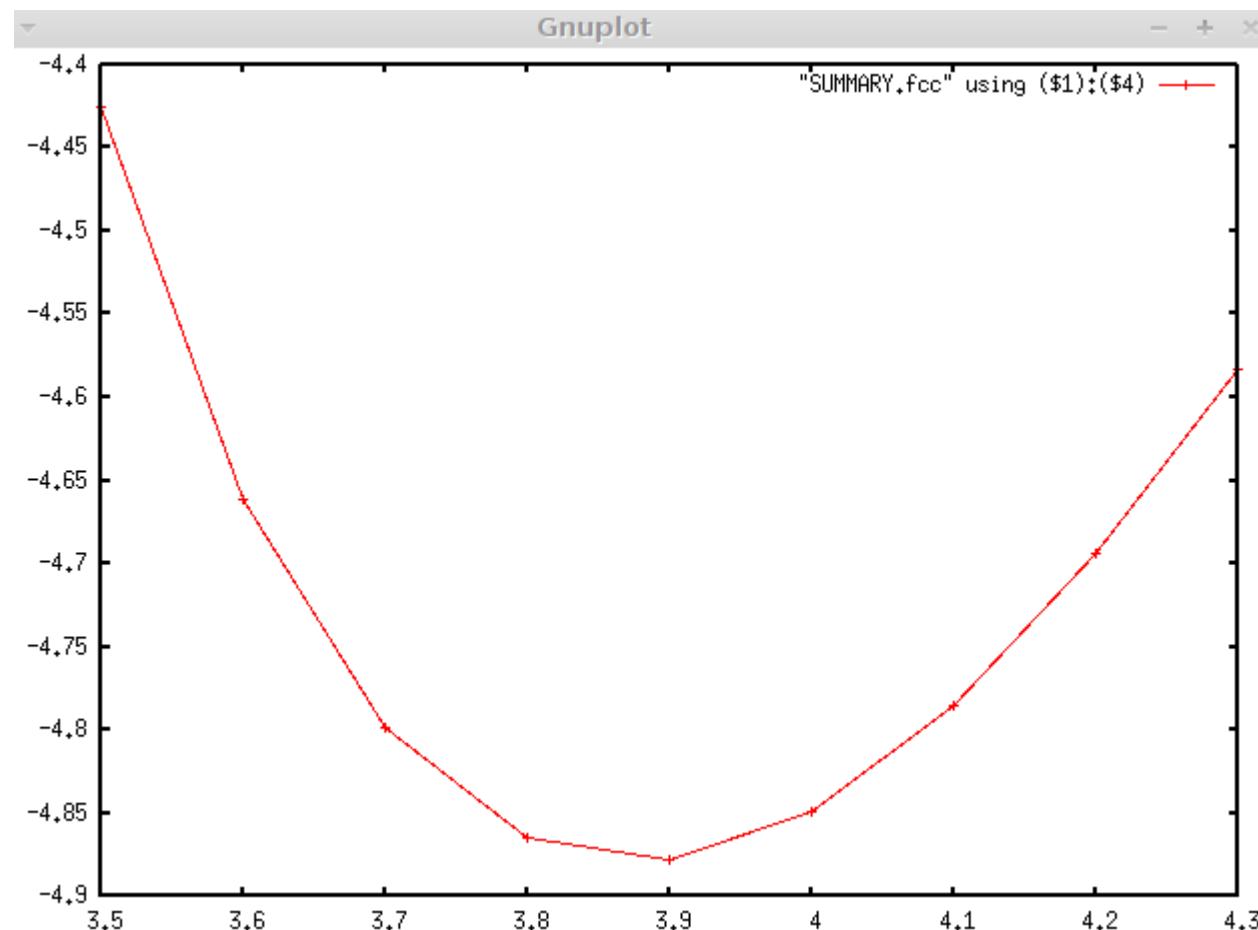
Equilibrium volume of fcc Si (Example: 2_1_fccSi)

A quick look at the results? (see README)

```
>gnuplot
```

```
gnuplot> plot "SUMMARY.fcc" using ($1):($4) w lp  
gnuplot> exit
```

“kill the window with”



Density-of-states of fcc Si (Example: 2_2_fccSi_dos)

- perform a static (`NSW=0`, `IBRION=-1`) self-consistent calculation → DOS in `DOSCAR`
- large system
 1. convergence with a small number of kpoints
 2. for DOS; increase the number of kpoints and set `ICHARG=11`, charge-density (`CHGCAR`) from the last self-consistent run
 - `ICHARG=11` treats all k-points independently
 - charge density and the potential fixed
 - → Bandstructure

Density-of-states of fcc Si (Example: 2_2_fccSi_dos)

general:

```
System = fcc Si
ICHARG=11 #charge read file
ENCUT  =    240
ISMEAR = -5 #tetrahedron
```

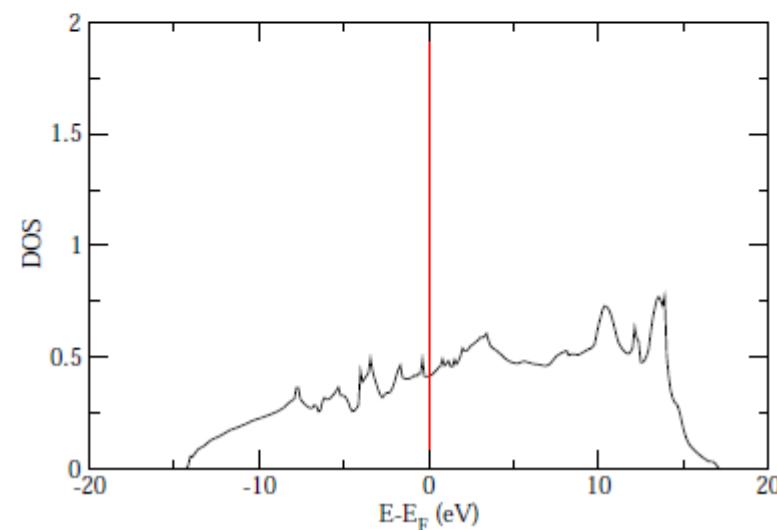
K-Points

```
0
Monkhorst Pack
21 21 21
0 0 0
```

INCAR

- read CHGCAR from previous run
- set smearing to fit the problem

KPOINTS



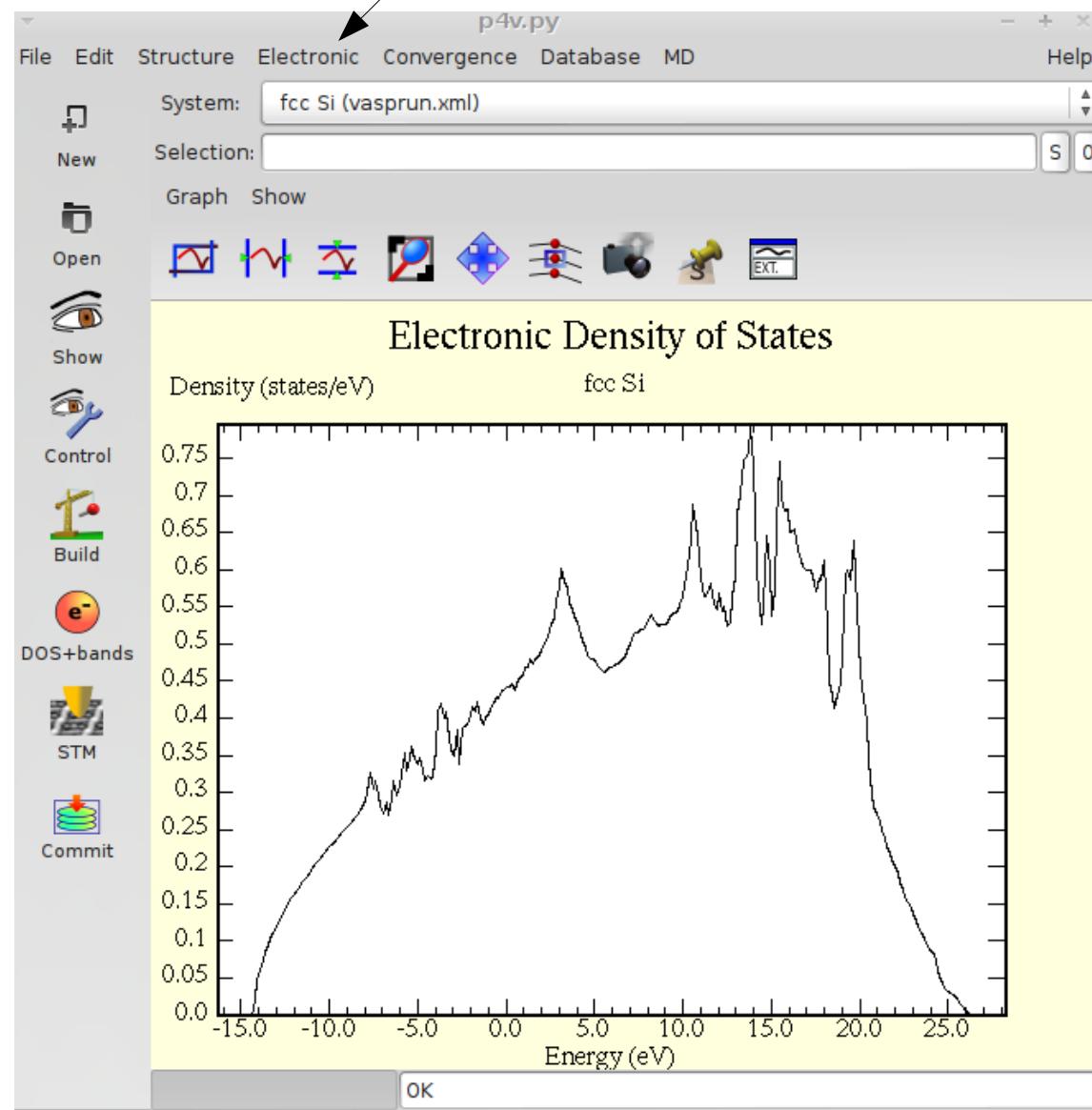
N.B. To copy the self-consistent charge density of example 2_1_fccSi to your current working directory (assumed to be 2_2_fccSi_dos), type: `$ cp/2_1_fccSi/CHGCAR` .

You must do this otherwise VASP can not read the CHGCAR and will terminate

Density-of-states of fcc Si (Example: 2_2_fccSi_dos)

Start p4vasp:
> p4v [vasprun.xml]

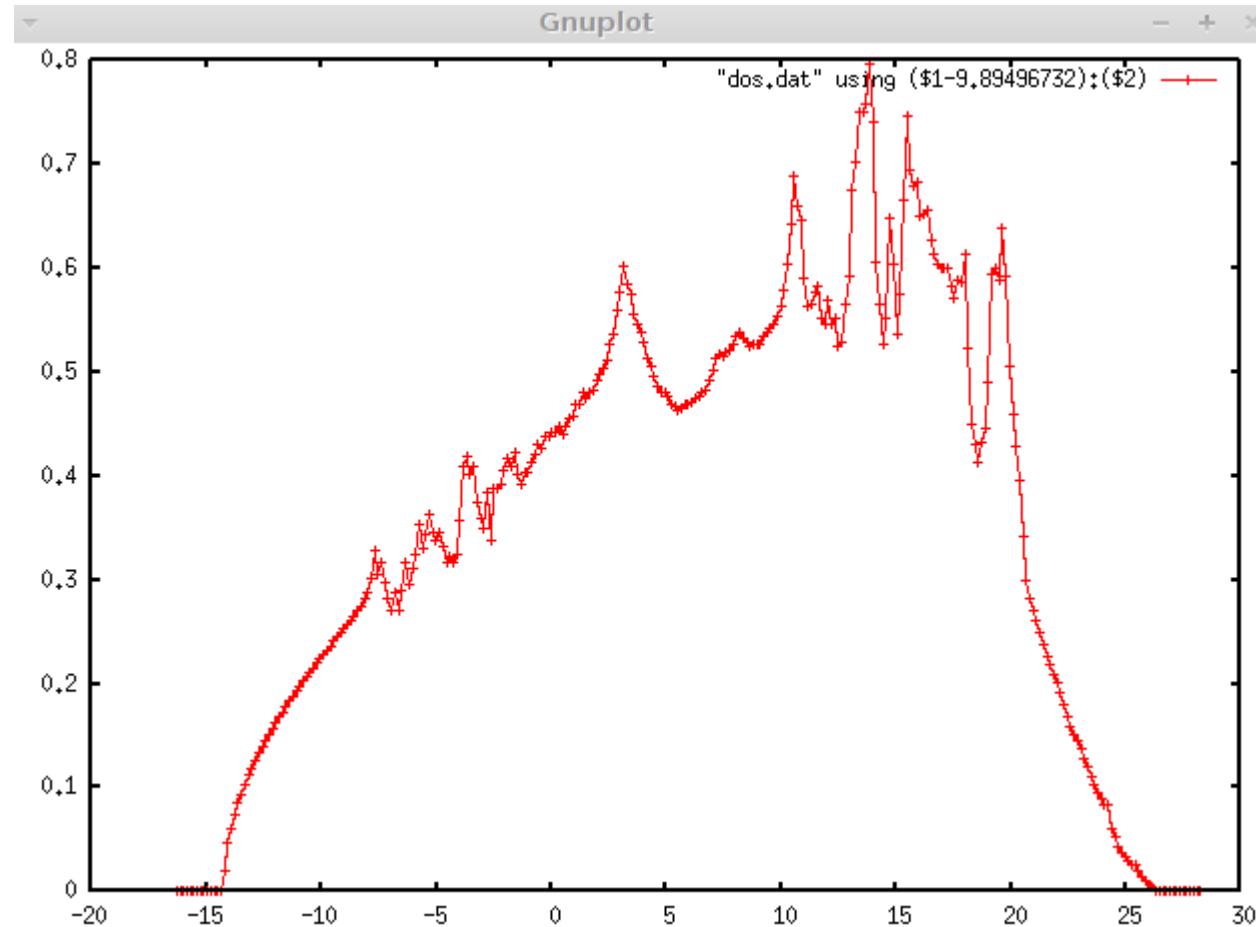
Go to: Electronic/DOS+bands



Density-of-states of fcc Si (Example: 2_2_fccSi_dos)

Or use gnuplot for a quick look:

```
>./plotdos
```

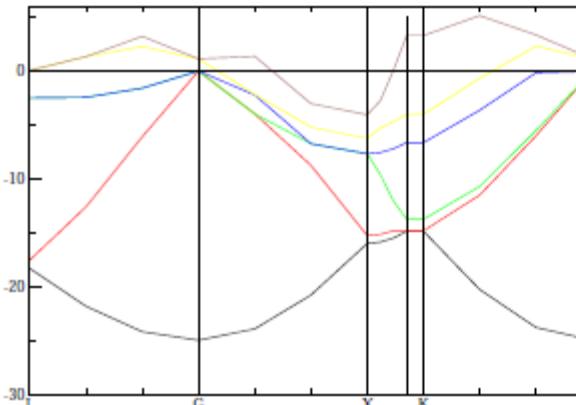


Bandstructure of fcc Si (Example: 2_3_fccSi_band)

```
kpoints for bandstructure L-G-X-U K-G  
10  
line  
reciprocal  
0.50000 0.50000 0.50000 1  
0.00000 0.00000 0.00000 1  
  
0.00000 0.00000 0.00000 1  
0.00000 0.50000 0.50000 1  
  
0.00000 0.50000 0.50000 1  
0.25000 0.62500 0.62500 1  
  
0.37500 0.7500 0.37500 1  
0.00000 0.00000 0.00000 1
```

KPOINTS

- k-points along line $\bar{L} - \bar{\Gamma} - \bar{X} - \bar{U}\bar{K} - \bar{\Gamma}$
- 10 points per line
- keyword `line` to generate bandstructure
- in reciprocal coordinates
- all points with weight 1



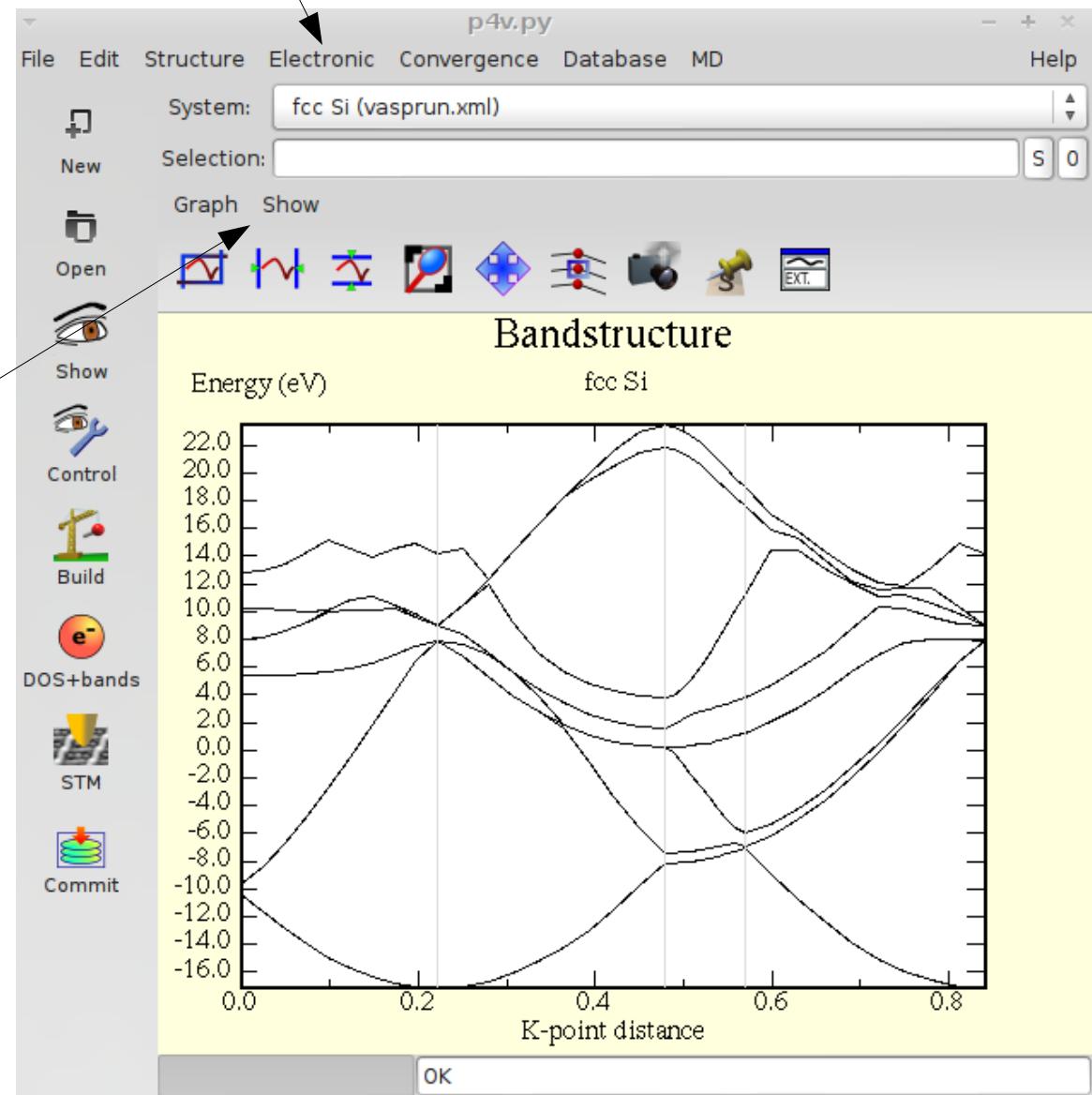
N.B. To copy the self-consistent charge density of example 2_1_fccSi to your current working directory (assumed to be 2_2_fccSi_band), type: `$ cp ../../2_1_fccSi/CHGCAR .`

You must do this otherwise VASP can not read the CHGCAR and will terminate

Bandstructure of fcc Si (Example: 2_3_fccSi_band)

Start p4vasp:
> p4v [vasprun.xml]

Step 1.) Go to: Electronic/DOS+bands



Step 2.) Go to: Show/Bands

Equilibrium volume of cd Si (Example: 2_4_diamondSi)

To Do:

- 1.) Determine equilibrium lattice constant / volume
- 2.) Calculate DOS (at groundstate volume)
- 3.) Compute bandstructure (at groundstate volume)

Job scripts:

- 1.) loop.job
- 2.) dos.job
- 3.) band.job

Visualisation: as in examples 2_1_fccSi, 2_2_fccSi_dos, and 2_3_fccSi_band

N.B.; have a look at README, and take a look at what the script do!

Equilibrium volume of cd Si (Example: 2_4_diamondSi)

```
5.1 1 F= -.10222147E+02 E0= -.10221786E+02 d E =-.721447E-03  
5.2 1 F= -.10517565E+02 E0= -.10517500E+02 d E =-.129988E-03  
5.3 1 F= -.10704095E+02 E0= -.10704088E+02 d E =-.130462E-04  
5.4 1 F= -.10797653E+02 E0= -.10797653E+02 d E =-.832225E-06  
5.5 1 F= -.10814441E+02 E0= -.10814441E+02 d E =-.409086E-07  
5.6 1 F= -.10766003E+02 E0= -.10766003E+02 d E =-.223801E-08  
5.7 1 F= -.10664898E+02 E0= -.10664898E+02 d E =-.108197E-09
```

SUMMARY.diamond

- Energy vs. lattice parameter
 $a = 5.465 \text{ \AA}$
- for DOS and band-structure rounded to
 $a = 5.5 \text{ \AA}$

cubic diamond

5.5

0.0	0.5	0.5
0.5	0.0	0.5
0.5	0.5	0.0

2

Direct

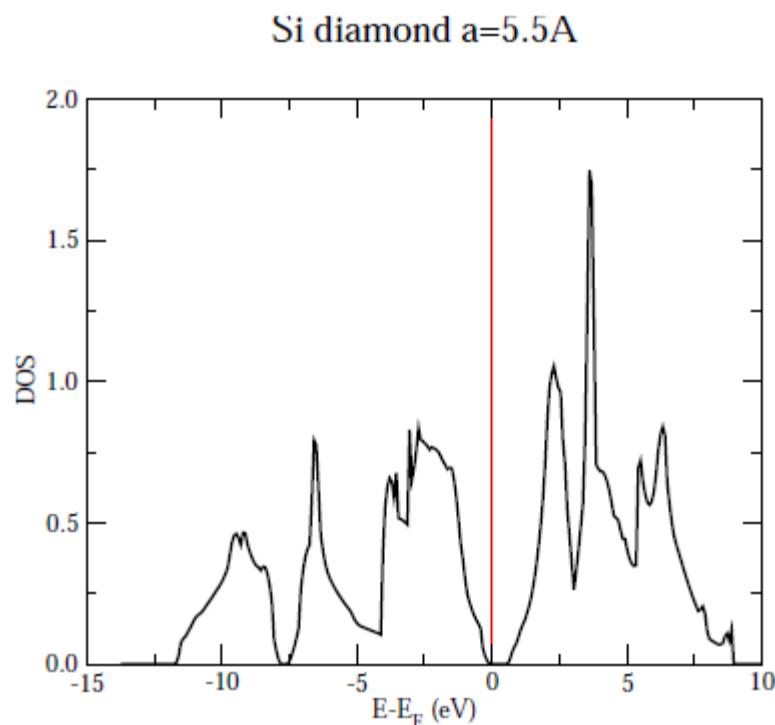
-0.125	-0.125	-0.125
0.125	0.125	0.125

POSCAR

- diamond Si lattice constant 5.5 Å
- fcc cell
- 2 atoms in cell
- calculate energy vs. lattice parameter
 - volume scan with a script

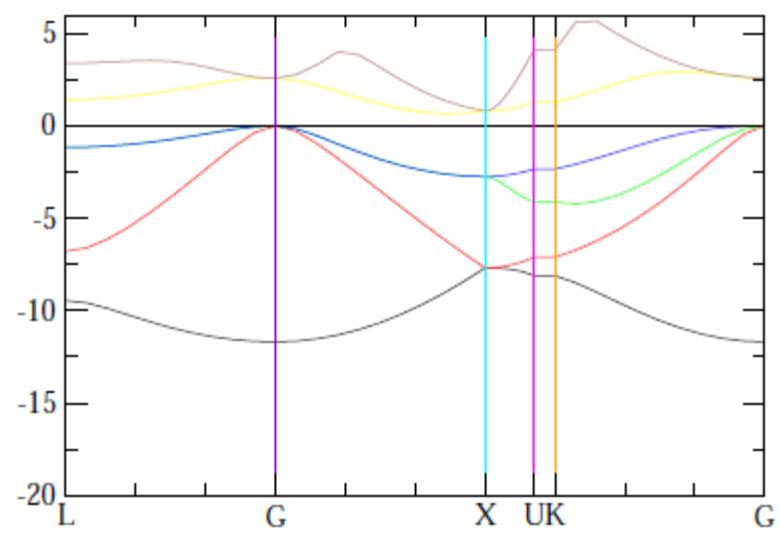
Equilibrium volume of cd Si (Example: 2_4_diamondSi)

Density of States



Bandstructure

Bandstructure Si diamond



“Fat” bands (Example: 2_4_diamondSi)

Start p4vasp:

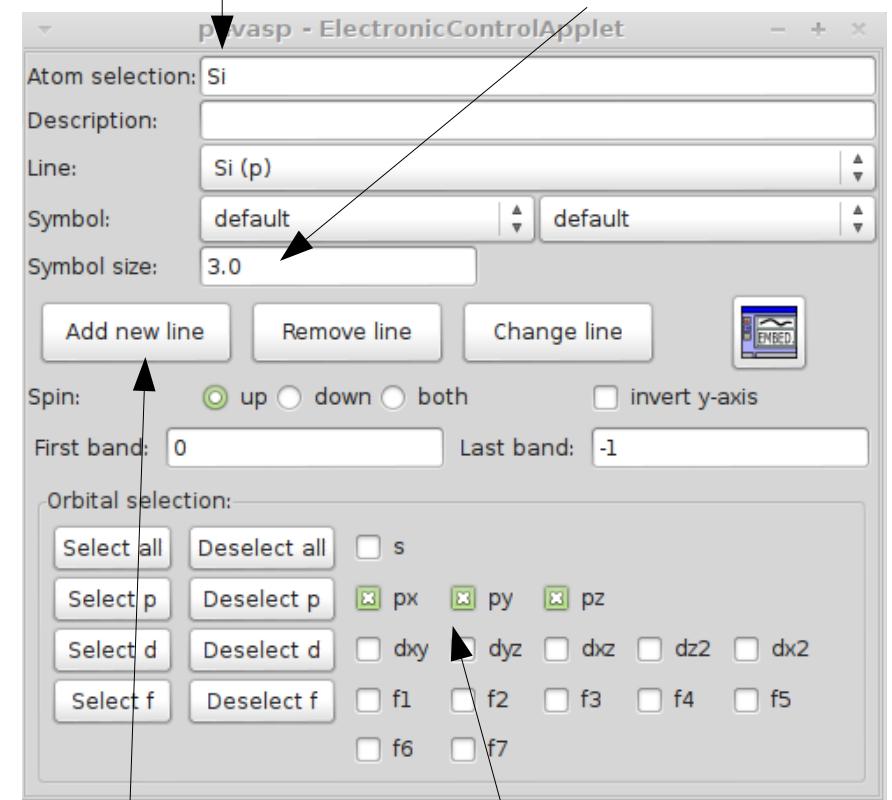
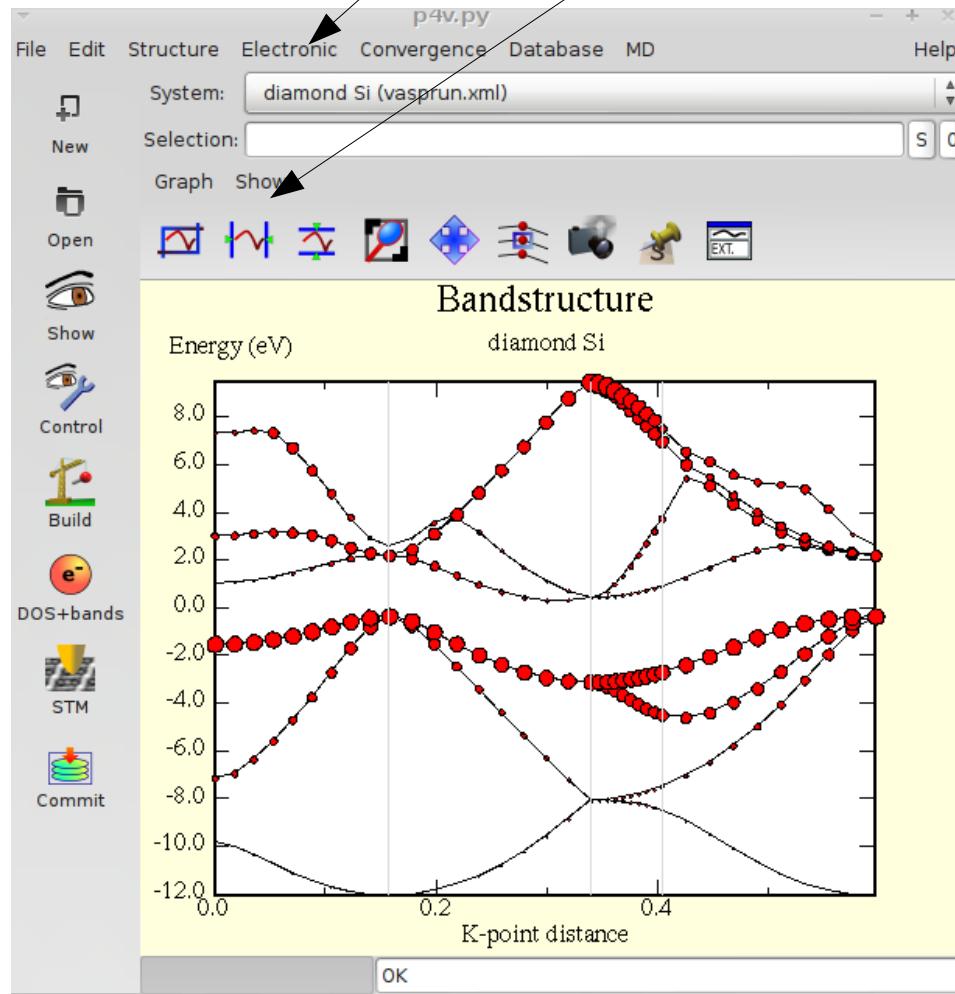
> p4v [vasprun.xml]

Step 1.) go to:
Electronic/Local DOS+bands control

Step 2.) Go to: Show/Bands

Step 3.) select atoms: “all”, “Si”, “1”, “2”, ...

Step 4.) adjust symbol size



Step 5.) select orbital character
Step 6.) and “add new line”

Volume relaxation of cd Si (Example: 2_5_diamondSi_volrel)

To determine the equilibrium volume we can:

- fit the energy over a certain volume range to an equation of states (e.g. a Murnaghan equation of states)

Alternatively, we will now try:

- relaxing the structure with vasp
 - IBRION=2 conjugate-gradient algorithm
 - ISIF=3 change internal parameters & shape & volume

```
System = diamond Si
ISMEAR = 0; SIGMA = 0.1;
ENMAX  = 400
IBRION=2; ISIF=3 ; NSW=15
EDIFF   = 0.1E-05
EDIFFG  = -0.001
```

- NSW=15 15 steps of ionic relaxation
- increase accuracy of electronic steps
- forces on ions smaller than 0.001 eV/Å

Volume relaxation of cd Si (Example: 2_5_diamondSi_volrel)

```
-----  
Total      0.00155    0.00155    0.00155    0.00000    0.00000    0.00000  
in kB      0.06065    0.06065    0.06065    0.00000    0.00000    0.00000  
external pressure =          0.06 kB  Pulay stress =        0.00 kB
```

'OLUME and BASIS-vectors are now :

```
-----  
energy-cutoff :      400.00  
volume of cell :     40.88
```

- from equation of state $a = 5.4687 \text{ \AA}$
(volume scan + Murnaghan EOS: ENMAX = 400!)
- relaxing the structure $a = 5.4684 \text{ \AA}$
- difference can be due to the Pulay stress
(especially when the relaxation starts far away from equilibrium)
 - increase the plane wave cutoff by at least 30%
(here we used ENMAX = 400 instead of 240!)
 - use small EDIFF

Volume relaxation of cd Si (Example: 2_5_diamondSi_volrel)

Crystal Structure Optimization (Summary)

- calculation of the equilibrium volume
 - fit the energy over a certain volume range to an equation of states
 - when internal degrees of freedom exist (e.g. c/a), the structure must be optimized
 - IBRION = 2 conjugate-gradient algorithm
 - at each volume NSW = 10 e.g. 10 ionic steps
 - ISIF=4 change internal parameters & shape
- simpler but less reliable: relaxing all degrees of freedom including volume
 - to relax all degrees of freedom use:
ISIF=3 change internal parameters & shape & volume
 - mind Pulay stress problem
increase cutoff by 25-30% when the volume is allowed to change

Ionic relaxation in cd Si (Example: 2_6_diamondSi_rel)

general:

```
System = diamond Si
START = 0 ; ICHARG=2
ENCUT = 240
ISMEAR = 0; SIGMA = 0.1;
NSW = 10; IBRION = 2
ISIF = 2

EDIFFG = -0.0001
```

INCAR

- NSW = 10 ionic relaxation, 10 steps
- IBRION = 2: conjugate-gradient algorithm
- ISIF=2 relax internal parameters

Ionic relaxation in cd Si (Example: 2_6_diamondSi_rel)

fcc:

5.5

0.0 0.5 0.5
0.5 0.0 0.5
0.5 0.5 0.0

2

Direct

-0.125 -0.125 -0.130
0.125 0.125 0.130

POSCAR

- standard diamond structure
→ break symmetry
- change z positions
from 0.125 → 0.130

after 10 steps:

POSITION			TOTAL-FORCE (eV/Angst)		
4.81253	4.81253	4.81250	-0.000724	-0.000724	-0.000031
0.68747	0.68747	0.68750	0.000724	0.000724	0.000031
total drift:			0.000000	0.000000	0.000000

General comments

- files to watch during relaxations
 - STDOOUT (Terminal), each electronic step is written to the terminal
 - OSZICAR a copy of the Terminal output
 - OUTCAR more detailed information on every electronic and ionic step
- other important files
 - CONTCAR holds the structure of the last ionic step,
the structural result (also very important for restarting a relaxation)
 - STOPCAR stops a relaxation

fcc Ni (Example: 2_7_fccNi)

General setup:

```
general:  
    SYSTEM = fcc Ni  
    ISTART = 0 ; ICHARG=2  
    ENCUT = 270  
    ISMEAR = 1 ; SIGMA = 0.2
```

```
spin:  
    ISPIN=2  
    MAGMOM = 1
```

K-Points

0

Monkhorst-Pack

11 11 11
0 0 0

INCAR

- startjob; initial charge-density from overlapping atoms
- energy cut-off: 270 eV (default)
- MP-smearing (metal!)
- spinpolarized calculation initial moments of 1
- static calculation

KPOINTS

- equally spaced mesh, 56 kpoints
- odd → centered at Γ

fcc Ni (Example: 2_7_fccNi)

To Do:

- 1.) Determine equilibrium lattice constant / volume
- 2.) Calculate DOS (at groundstate volume)
- 3.) Compute bandstructure (at groundstate volume)

Job scripts:

- 1.) loop.job
- 2.) dos.job
- 3.) band.job

Visualisation: as in examples 2_1_fccSi, 2_2_fccSi_dos, and 2_3_fccSi_band
But beware there are separate spin-up and spin-down states!

N.B.; have a look at README, and take a look at what the script do!

fcc Ni (Example: 2_7_fccNi)

